

**SILICONE-MODIFIED POLYESTER TOPCOAT COMPOSITION**

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**Abstract**

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**PURPOSE:**The titled composition with excellent coating property, luster, etc., obtd. by mixing a binder component consisting of a specified silicone-modified polyester, an aminoaldehyde resin and/or blocked isocyanate, with a pigment.

**CONSTITUTION:**A binder component consisting of (A) 60-90pts.wt. silicone- modified polyester obtd. by the modification of 75-97pts.wt. oil-free saturated polyester resin of hydroxy value 60-200, contg. acid components, of which at least 25mol% consists of a saturated alicyclic polybasic acid (e.g., hexahydrophthalic acid or hexahydrotrimellitic acid), by use of 25-3pts.wt. reactive organopolysiloxane resin of MW about 500-2,000 and (B) 40-10pts.wt. aminoaldehyde resin and/or blocked isocyanate, is mixed with (C) 3-100PHR pigment to prepare the purpose paint composition. The paint is suitable for the topcoating of an automobile body.

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## SPECIFICATION

1. Title of the Invention: SILICONE-MODIFIED POLYESTER TOP-COAT PAINT COMPOSITION

### 2. Claims

1. A silicone-modified polyester topcoat composition, comprising, as its essential components, (A) a silicone-modified polyester, (B) a binder component consisting of amino-aldehyde resin and/or block isocyanate, and (C) a pigment, wherein: at least 25 mol% of an acid component of the polyester of the component (A) is a saturated alicyclic polybasic acid; the component (A) is obtained by modifying 75-97 parts by weight of an oil-free saturated polyester resin whose hydroxyl value is 60-200 with 3-25 parts by weight of a reactive organopolysiloxane resin whose molecular weight is about 500 to about 2,000; the content ratio between the component (A) and the component (B) is 60-90 parts by weight of (A) for 10-40 parts by weight of (B); and the pigment content is 3-100 PHR.

2. A composition according to claim 1, wherein the acid component of the polyester comprises not only the saturated alicyclic polybasic acid but also one selected from the group consisting of an aromatic polybasic acid and a linear-chain saturated dibasic acid represented by the general formula  $\text{HOOC}(\text{CH}_2)_n\text{COOH}$  (where n is an integer of 1-12).

3. A composition according to claim 2, wherein the total amount of the saturated alicyclic polybasic acid and the aromatic polybasic acid is 70 mol% or more, and the content of the aromatic polybasic acid is 55 mol% or less.

### 3. Detailed Description of the Invention

The present invention relates to a topcoat paint composition for use in spray coating, comprising silicone-modified polyester/amino-aldehyde resin and/or block isocyanate.

Amino-alkyd resin paints, amino-acrylic resin paints, acrylic lacquer paints, and the like, are conventionally known in the art as topcoat paints for automobile bodies. The amino-alkyd resin paints are characterized in that they are easy to apply and have good finish appearance (the gloss of the applied film, the thick touch, etc.), and a good weather resistance for high pigment concentration ranges (the gloss retention). However, a so-called "dark color" coating film, i.e., a coating film in which the pigment concentration is low and the pigment contains a large amount of pigment other than white (hereinafter, referred to as a "coloring pigment") has a poor waxing resistance as will be discussed below. That is, when waxing on such a coating film, the film is likely to get scratched or lose its gloss, and the waste cloth used for waxing is likely to get colored considerably. While the waxing resistance is required in a coating film immediately after application thereof and after outdoor exposure thereof, it is difficult to obtain a satisfactory waxing resistance with an amino-alkyd resin topcoat paint. The amino-acrylic resin topcoat paint is quite desirable in its weather resistance for low pigment concentration ranges (40-30 PHR or less), but the waxing resistance before exposure is not always desirable. Especially, it is difficult to satisfy the requirements such

as the properties required for a topcoat on an automobile body, i.e., non-sand interlayer adhesion (i.e., the adhesion between two coating films when the first coat is applied and baked, after which the same paint is again applied and baked onto the first coat for touchup), the Erichsen test, the shock resistance, and the finish appearance (the gloss of the applied film, the thick touch, etc.). The acrylic lacquer paints have a significantly low as-applied solid component concentration, and it is necessary to provide many application steps.

Oil-free polyester/amino-aldehyde resin paints have advantages over the above-described paints such as a good weather resistance, good mechanical properties in the applied film (the Erichsen test, the shock resistance), a good interlayer adhesion, and a high as-applied solid component concentration. However, it has been believed that it is difficult to use such paints particularly as a topcoat on an automobile body because: it is difficult to apply (e.g., repelling is likely to occur); the surface of the applied film is "blurred", so to speak, and the gloss is poor; and the compatibility with an amino resin is poor.

It has been proposed (Japanese Patent Application No. 54-94269) to use an oil-free polyester resin having a special composition to obtain an oil-free polyester/amino-aldehyde resin topcoat paint with improvements in terms of the gloss, repelling resistance, compatibility with an amino resin, and the ease of application (i.e., the application property).

An object of the present invention is to provide a topcoat paint composition which has the advantages of oil-free polyesters and in which the application property, the gloss of the applied film, the repelling resistance, etc., (particularly, the application property) are further im-

proved from those of the above-described paint in the prior art.

The object of the present invention is realized by a silicone-modified polyester topcoat composition, comprising, as its essential components, (A) a silicone-modified polyester, (B) a binder component consisting of amino-aldehyde resin and/or block isocyanate, and (C) a pigment, wherein: at least 25 mol% of an acid component of the polyester of the component (A) is a saturated alicyclic polybasic acid; the component (A) is obtained by modifying 75-97 parts by weight of an oil-free saturated polyester resin whose hydroxyl value is 60-200 with 3-25 parts by weight of a reactive organopolysiloxane resin whose molecular weight is about 500 to about 2,000; the content ratio between the component (A) and the component (B) is 60-90 parts by weight of (A) for 10-40 parts by weight of (B); and the pigment content is 3-100 PHR.

The excellent application property of the paint composition of the present invention has been achieved mainly due to a successful and balanced suppression of the undesirable phenomena of "running" and "bubbling" which may occur in paint application.

Generally, the term "running" refers to a phenomenon where a paint which is applied onto a vertically standing painting substrate by, for example, spray application, runs down along the substrate due to gravity. A paint applied onto a painting substrate is required to stay where it is applied without having the running phenomenon. Otherwise, the film thickness will be substantially uneven, or a flow pattern occurs on the application surface, whereby a desirable application surface cannot be obtained.

The occurrence of such a running phenomenon rapidly increases as the thickness of the applied film increases over a certain value. The thickness past which the occurrence of running rapidly increases is called the "running critical thickness". A paint having a higher running critical thickness is considered to have a good application property, in other words, it is a paint which is easy to apply.

The term "bubbling" refers to a phenomenon where a baking-finish-type paint, after it is taken out of a baking furnace, has an indicative trace of a bubble or a bubble itself on the application surface. It is believed that bubbling occurs due to rapid evaporation of a solvent in the paint during baking or passage of an air bubble which has been trapped during application. The occurrence of this phenomenon also rapidly increases when the thickness of the applied film increases over a certain value. Such a critical thickness is called the "bubbling critical thickness". The higher this value is, the better the application property is.

Thus, a paint having a high running critical thickness and a high bubbling critical thickness is an easy-to-apply paint. However, the two values are typically in a trade-off relationship, and it is in many cases difficult to have both values high. In other words, if one of the values is increased, the other will decrease, and it is difficult to obtain a paint which has both values high. For example, the bubbling critical thickness can be increased by using a large amount of a solvent which has a high boiling point and is less likely to evaporate. However, this slows down the viscosity increase rate of the applied paint, and as a result the applied paint is more likely to run, thereby lowering the running critical thickness.

Typically, with an oil-free polyester, as compared with an alkyd resin or an acrylic resin, it is difficult to maintain a high level and good balance of running and bubbling. However, when a particular oil-free polyester is modified with a small amount of silicon resin according to the present invention, surprisingly, it is possible to obtain a high level and good balance of running and bubbling.

Silicone-modified polyester or silicone-modified alkyd resins have conventionally been used as a pre-coat metal paint (e.g., Japanese Laid-Open Publication No. 47-21493). However, such a conventional silicone-modified resin comprises a large amount, 30 wt% or more, of a silicone resin so as to improve the heat resistance and the weather resistance of the resin paint.

On the contrary, the present invention significantly improves the application property of a spray topcoat paint by modifying a particular polyester with a small amount of silicone.

An oil-free polyester to be a substrate resin of a silicone-modified polyester for use with the present invention is characterized in that it comprises a saturated alicyclic polybasic acid (a) in an amount of at least 25 mol%, and preferably at least 40 mol%, of the total acid component. The other acid component, i.e., the polybasic acid material, of the polyester may be an aromatic polybasic acid (b) and/or a linear-chain saturated dibasic acid (c) represented by the general formula  $\text{HOOC}(\text{CH}_2)_n\text{COOH}$  (where n is an integer of 1-12). Moreover, in order to prepare a preferable substrate polyester, it is desirable that the total amount of the polybasic acid components (a) and (b) is 70 mol% or more and that the content of the component (b) is 55 mol% or more.

When the total amount of the polybasic acid components (a) and (b) is less than 70 mol%, the weather resistance and/or the acid resistance decrease. When the content of the component (b) exceeds 55 mol%, the compatibility between the substrate polyester and the silicone resin as a modifier may decrease, thereby making it more difficult for the reaction to modify an oil-free polyester with a silicone resin to progress. Moreover, the compatibility between the produced silicone-modified polyester and the amino-aldehyde resin as a crosslinking agent decreases, thereby causing deficiencies on the application surface (insufficient gloss) and/or decreasing the solvent resistance.

The hydroxyl value of the oil-free polyester is required to be in the range of 60-200, and preferably in the range of 80-150. When the value is less than or equal to 60, the applied film will not be cured sufficiently. When the value is equal to or greater than 200, the dispersibility of the pigment and the compatibility thereof with a crosslinking agent decrease.

Examples of the saturated alicyclic polybasic acid (a) forming the oil-free polyester used in the present invention include hexahydroisophthalic acid, hexahydroterephthalic acid, hexahydrophthalic acid and anhydride thereof, a methylhexahydrophthalic acid and anhydride thereof, hexahydrotrimellitic acid and anhydride thereof, hexahydro-2-methyltrimellitic acid and anhydride thereof, and the like. Examples of the aromatic polybasic acid (b) include phthalic acid and anhydride thereof, isophthalic acid, terephthalic acid, dimethylisophthalic acid, dimethylterephthalic acid, trimellitic acid and anhydride thereof, pyromellitic acid and anhydride thereof, and the like. The examples of the linear-chain saturated dibasic acid (c) represented by the general formula  $\text{HOOC}(\text{CH}_2)_n\text{COOH}$  include succinic acid (and

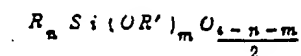


anhydride thereof), adipic acid, pimelic acid, azelaic acid, sebacic acid, brassylic acid, and the like.

On the other hand, the alcohol component of the oil-free polyester is not so limited and may be those that are commonly used in the prior art for producing a polyester. For example, ethylene glycol, diethylene glycol, propylene glycol, neopentyl glycol, 1,2-butylene glycol, 1,3-butylene glycol, 2,3-butylene glycol, 1,4-butylene glycol, 1,6-hexanediol, 1,5-pentanediol, 1,6-hexanediol, 2,5-hexanediol, trimethylolethane, trimethylolpropane, glycerin, pentaerythritol, dipentaerythritol, diglycerin, sorbitol ester diol 204 (manufactured by Union Carbide Corporation (U.S.)), tri-cyclodecanedimethanol, 1,4-cyclohexanedimethanol, and the like, are contemplated.

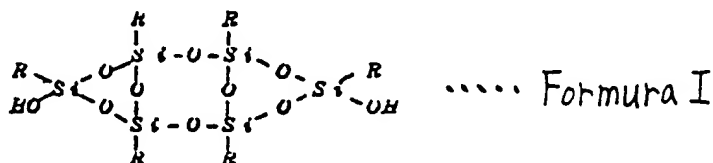
The oil-free polyester to be a substrate resin of a silicone-modified polyester can be produced by a common condensation polymerization of the saturated alicyclic polybasic acid (a) and the aromatic polybasic acid (b), and optionally the linear-chain saturated dibasic acid (c), with at least one of the above-listed alcohols. In this process, the molecular weight may be adjusted by using, for example, benzoic acid, p-t-butyl benzoic acid, methyl benzoate, or the like, as a terminal blocking agent. The reaction ratio between the polybasic component and the alcohol component is adjusted so that the hydroxyl value of the obtained oil-free polyester is 60-200, and preferably 80-150.


The silicone resin used in the present invention to modify the substrate polyester is an organopolysiloxane resin having a number average molecular weight of about 500 to about 2000 which is represented by the following unit formula:

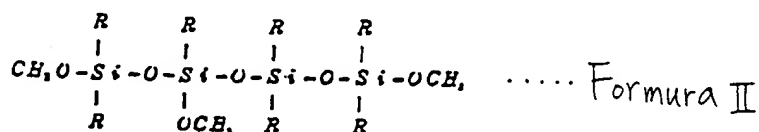



where R denotes a monovalent organic group which binds to silicon via carbon-silicon bond, R' denotes hydrogen, an alkyl group or an aryl group of C<sub>1</sub>-C<sub>20</sub>. In the above formula, each of n and m is a number less than or equal to 4, and n+m has to be less than or equal to 4.

The silicone resin used in the present invention preferably includes, in each molecule, two or more of the reactive group such as a hydroxyl group or an alkoxy group represented by (OR') in the above formula. Such a silicone resin includes Z-6018 (manufactured by Dow Corning, molecular weight: 1600, a definition of R represented by Formula I)



[R denotes CH<sub>3</sub> or  ], and Z-6188 (manufactured by Dow Corning, molecular weight: 650, a definition of R represented by Formula II)



[R denotes CH<sub>3</sub> or  ], as well as Sylkyd 50, DC-3037 (manufactured by Dow Corning), KR-216, KR-218, KSP-1 (manufactured by Shinetsu Silicone), TSR-160, TSR-165 (manufactured by Toshiba), SH5050, SH6018, SH6188 (manufactured by Toray Silicone), and the like.

When producing a silicone-modified polyester by modifying a substrate polyester with a silicone resin according to the present invention, the amount of the silicone

resin to be used is, in terms of the ratio between the substrate polyester and the silicone resin, 3-25 parts by weight for 97-75 parts by weight of the substrate polyester, and preferably 7-18 parts by weight for 93-82 parts by weight of the substrate polyester. When the content of the silicone resin is 3 parts by weight or less, the pigment dispersibility, which is an advantage of the silicone-modified polyester, decreases, thereby causing deficiencies such as blurring of the application surface, and reducing the application workability, e.g., repelling is likely to occur. On the other hand, when the content of the silicone resin is 25 parts by weight or more, the resin cost becomes high, and the alkali resistance and the curing property decrease, thereby losing its suitability as a topcoat paint.

The silicone-modified polyester used in the present invention can be produced by using a method which is per se known in the art to copolymerize the substrate polyester and the silicone resin at the above-described ratio. The reaction is suitably performed in the presence or absence of a solvent by heating the materials to a temperature of 200°C or less, and preferably 150°C or less. As the solvent used herein, a solvent which is commonly used in a paint such as aromatic solvents, esters, ketones, petroleums, or the like, may be selected in view of the relationship between the boiling point thereof and the co-condensation reaction temperature. An alcohol solvent is not preferred because it reduces the rate of the co-condensation reaction. It is preferred to use a condensation catalyst in order to promote the co-condensation reaction. The condensation catalyst used herein may be iron octenoate, zinc octenoate, potassium hydroxide, p-toluenesulfonic acid, tin(II) octenoate, tetraalkyl titanate, hydrochloric acid, phosphoric acid, a higher fatty acid, maleic anhydride, or the like.

The present invention significantly improves the application property by using as a topcoat paint resin a silicone-modified polyester which is obtained by modifying a particular polyester with a small amount of silicone resin (3-25 wt%) as described above. The application property as used herein refers to an increased bubbling and/or running critical thickness as the applied film is cured by heating, and to a property of preventing repelling and/or indentation when a heterologous dust (e.g., amino-alkyd resin paint, or an amino-acrylic resin paint) is put on an uncured applied film before the heat-drying process. The silicone modification also has other advantages, associated with the above advantages, e.g., an increase in the dispersibility of a pigment, an increase in the compatibility and solubility with a solvent and thus an increase in the solid component concentration in the spray application. Moreover, with the topcoat paint of the present invention, the gloss and the vividness of the applied film are much better than those of a conventional oil-free polyester topcoat paint. Such advantages are achieved only by using a resin obtained by modifying a polyester having a particular composition disclosed herein with an amount of silicone in the range of 3-25 wt%. The topcoat paint of the present invention is especially desirable as a topcoat paint for automobiles. When a polyester having a composition other than those specified herein is modified with a silicone, there would only be little improvement in the application property, and a sufficient practicability as a topcoat paint for automobiles cannot be obtained.

The amino-aldehyde resin used in the present invention as the crosslinking component (B) may be any of most amino-aldehyde resins commonly used as a paint, and the amino component thereof may be melamine, urea, benzoguanamine, acetoguanamine, steroguanamine, spiroguanamine, or the like. In view of the weather resistance, the most preferred resin

is a melamine formaldehyde resin. A common curing catalyst may be added to such an amino-aldehyde resin in order to lower the curing temperature.

The block-type polyisocyanate may be produced by turning yellowing-free polyisocyanate into a block-type polyisocyanate with a common blocking agent such as, for example, an aliphatic or aromatic monoalcohol, phenol, oxime, or caprolactam. For example, Takenate B-815N (manufactured by Takeda Chemical Industries, Co., Ltd.), Takenate B-840N (manufactured by Takeda Chemical Industries, Co., Ltd.), Ad-duet B1065 (Veba Chemie (Germany)), or ADDITOL VXL-80 (manufactured by Hoechst Japan Ltd.) may be used. When such a block-type polyisocyanate is used, a catalyst for facilitating the dissociation of a blocking agent may be optionally added.

The above-described amino-aldehyde resin and the block-type polyisocyanate may be used alone or in combination.

The binder component composition in the paint composition of the present invention needs to be in the range of 90/10-60/40 in terms of the weight ratio between the silicone-modified polyester and the amino-aldehyde resin and/or block-type polyisocyanate. When the content of the amino-aldehyde resin and/or block-type polyisocyanate as a crosslinking agent is below this range, the curing will be insufficient, thereby lowering the weather resistance, the hardness of the applied film, the solvent resistance, and the like. When the content of the crosslinking agent is above this range, the applied film will be brittle.

While the pigment concentration of the paint composition of the present invention may be 100 PHR or less, the concentration is typically required to be 3 PHR or more

in order to completely cover an underlying layer with a thickness (about 20-50  $\mu$ ) which is commonly employed with a topcoat paint for automobile bodies, or the like. When the concentration is 100 PHR or more, the weather resistance will be on the same level as that of an amino-alkyd resin topcoat paint, thereby detracting from the advantages of the present invention.

The paint composition of the present invention has a good waxing resistance before and after exposure and has a particularly desirable waxing resistance in the case where paint contains a large amount of coloring pigment. The effects of the present invention are particularly pronounced when the weight ratio of the coloring pigment/titanium white pigment in the pigment is in the range of 100/0-30/70, and preferably 100/0-60/40.

An automobile body can be painted with a paint composition of the present invention as follows. First, a paint is produced by a common method by mixing a binder component consisting of the silicone-modified polyester component (A) and the crosslinking component (B) with a commonly used coloring pigment, and optionally an additive. The produced paint is adjusted by a dilution solvent so that the paint viscosity is 20-30 sec as measured with a Ford cup No. 4 (20°C). Then, the paint is applied on a painting substrate having a first coat, and optionally a second coat, applied thereon so that the applied film after being dried has a thickness of about 20-60  $\mu$ . The application method may be a common air spray method, an airless spray method, electrostatic application method, or the like. Then, the applied paint is left standing at room temperature for a few minutes, after which it is heated to 80-160°C for 20-40 min, thereby obtaining a topcoat.

The silicone-modified polyester topcoat paint composition of the present invention has a level of performance comparable to that of an amino-alkyd resin paint, which is most commonly used as a topcoat for automobiles, in terms of the application property, the pigment dispersibility, the appearance of the applied film, the mechanical properties, the chemical resistance and the solvent resistance of the applied film, among other properties required for a topcoat on an automobile. For the weak points of an amino-alkyd resin paint, i.e., the weather resistance for low pigment concentration ranges (the gloss retention) and the waxing resistance before and after exposure, the paint composition of the present invention is much better than an amino-alkyd resin paint. Moreover, the paint composition of the present invention is also better than an amino-alkyd resin paint in terms of the interlayer adhesion. Furthermore, as compared to an amino-alkyd resin paint, the paint composition of the present invention is much superior in terms of the weather resistance (the gloss retention), the interlayer adhesion, the mechanical properties of the applied film. The paint composition of the present invention has a particularly desirable waxing resistance before and after exposure when used in a paint having a color which has a high chroma, e.g., dark green, dark maroon, or dark blue, which contains a large amount of a coloring pigment.

As described above, the paint composition of the present invention is significantly desirable in terms of the application property, the weather resistance and the pigment dispersibility. Therefore, beside automobile bodies, the paint composition of the present invention can be widely used in other household or industrial spray paints which are required to have a gloss in the applied film, the thick touch and the weather resistance.

The present invention will now be described by way of examples. In the examples, "parts" and "%" denote "parts by weight" and "wt%" unless otherwise noted.

#### Production Example 1

##### Production of oil-free polyester resin solution A

53.9 parts (0.35 mol) of hexahydrophthalic anhydride, 58.1 parts (0.35 mol) of isophthalic acid, 29.2 parts (0.2 mol) of adipic acid, 40.8 parts (0.3 mol) of trimethylolpropane, and 73.5 parts (0.7 mol) of neopentyl glycol are charged into a reaction chamber equipped with a heating device, a stirrer, a reflux device, a water separator, a rectifier and a thermometer, and heated. When the materials are melted so that they can be stirred, stirring is started, and the reaction chamber temperature is raised to 230°C. Herein, from 160°C to 230°C, the temperature is raised at a uniform rate for 3 hours, and generated condensation water is distilled out of the system.

When the temperature reaches 230°C, the temperature is kept constant and stirring is continued for 2 hours. Thereafter, xylol is added to the reaction chamber, and the reaction is switched to a condensation in the presence of a solvent, letting the reaction continue. When the acid value reaches 7, the reaction is terminated and the reaction chamber is cooled down. After the cooling, 100.6 parts of Suwazol #1500 (manufactured by Maruzen Sekiyu Kagaku) and 43.1 parts of cellosolve acetate were added to produce an oil-free polyester solution A. The oil-free polyester solution A had a solid component concentration of 60.0%, a varnish viscosity of V (Gardner viscosity, 25°C), an acid value of 7.0, and a hydroxyl value of 122.

#### Production Examples 2-10

##### Production of oil-free polyester resin solutions B-J



Using the material components as shown in Table 1, oil-free polyester resin solutions B-J were produced in a manner similar to that of Production Example 1. The varnish characteristic values of the solutions are shown in Table 1. The resin solutions A-F are used in the examples of the present invention, and solutions G-J are used in comparative examples.

Table 1

Production Example	2	3	4	5	6	7	8	9	10
Component	B	C	D	E	F	G	H	I	J
hexahydrophthalic anhydride	5.24 (0.34)	77.0 (0.5)	146.3 (0.95)	70.8 (0.46)	70.8 (0.46)	46.2 (0.3)	61.6 (0.4)	30.8 (0.2)	46.2 (0.3)
isophthalic acid	76.4 (0.46)	33.2 (0.2)		76.4 (0.46)	51.5 (0.31)	42.8 (0.3)	58.1 (0.35)	92.6 (0.6)	49.8 (0.3)
adipic acid	14.6 (0.1)	29.2 (0.2)			14.6 (0.1)	43.8 (0.3)	28.2 (0.2)	14.8 (0.1)	28.2 (0.2)
trimethylolpropane	34.0 (0.25)	34.0 (0.25)	61.2 (0.45)	40.8 (0.3)	62.6 (0.46)	40.8 (0.3)	13.6 (0.1)	40.8 (0.3)	68.0 (0.5)
neopentyl glycol	78.8 (0.75)	78.8 (0.75)	57.8 (0.55)	52.5 (0.6)	48.2 (0.44)	73.5 (0.7)	94.5 (0.9)	73.5 (0.7)	52.5 (0.6)
1,4-butylene glycol				18.0 (0.2)					
1,6-hexanediol					11.8 (0.1)				
p-t-butyl benzoic acid			35.6 (0.2)		17.8 (0.1)				
solid component concentration(%)	59.8	59.9	59.6	60.2	60.1	59.8	60.4	60.0	59.5
varnish viscosity	UV	TU	WX	Y	Q	WX	TU	X	L
acid value of resin	7.0	6.9	7.2	7.3	7.2	7.1	7.2	6.8	7.3
hydroxyl value of resin	105	110	68	104	130	124	49	122	227

Each number in ( ) denotes mol.

#### Production Example 11

##### Production of silicone polyester resin solution K

150.0 parts (solid component: 90) of the oil-free polyester resin solution A, 11.2 parts (solid component: 10) of silicone intermediate SH6188 (a silicone resin represented by Formula I above, manufactured by Toray Silicone), and TPT (A-1) (tetraisopropyl titanate, manufactured by Nippon Soda Co., Ltd.) as a condensation catalyst are charged into a reaction chamber equipped with a heating device, a stirrer, a water separator, and a thermometer, and heated while being stirred. When the reaction temperature reaches 140°C, the temperature is kept constant. Generated methanol is distilled out of the system. The reaction product is applied in a thin layer on a glass plate, and forcibly dried (130°C × 20 min). Both before the drying and after the drying, the reaction is continued until the resin is completely dissolved and becomes clear. At a point of time the resin is clear and the Gardner bubble viscosity is 4 sample or more higher than the initial viscosity (after cold mixing), the reaction is terminated and the reaction chamber is cooled down. After the cooling, 5 PHR of n-butanol and a mixed solvent of Suwazol #1500/cellosolve acetate=70/30 were added, and the solid component concentration is adjusted to 60%. The silicone polyester resin solution K had a solid component concentration of 59.8% and a varnish viscosity of X (Gardner viscosity, 25°C).

#### Production Examples 12-22

Silicone polyester resin solutions L-V were produced in a manner similar to that of Production Example 11 based on the resin contents shown in Table 2. The varnish characteristic values of the solutions are shown in Table 2. The resin solutions K-Q, U and V are used in the examples of the present invention, and the resin solutions R-T are used in the comparative examples. When producing silicone polyester solutions M and P, 11.4 parts of DC-3037 (a silicone

resin represented by Formula II above, manufactured by Dow Corning) is charged instead of 11.2 parts of silicone intermediate SH6188. Thereafter, the silicone polyester solutions M and P are produced in a manner similar to that of Production Example 11.

Table 2

content of resin solution resin solution	L	M	N	O	P	Q	R	S	T	U	V
name of polyester solution	B	C	D	E	F	G	H	I	J	A	A
content of silicone intermediate	1505	1503	1510	1495	1498	1505	1490	1500	1513	1523	1323
name of silicone intermediate	SH 6188	DC- 3037	SH 6188	SH 6188	DC- 3037	SH 6188	SH 6188	SH 6188	SH 6188	SH 6188	SH 6188
content of silicone intermediate	112	112	112	112	112	112	112	112	112	26	225
solid component concentration(%)	602	602	601	603	600	599	602	601	597	520	603
varnish viscosity	WX	V	Z	Z, Z <sub>2</sub>	T	ZZ <sub>1</sub>	U	Z <sub>2</sub>	P	X	YZ
amount of silicone modified(%)	10	10	10	10	10	10	10	10	10	5	20

### Production Example 23

#### Production of alkyd resin solution W

An alkyd resin solution W was produced in a manner similar to that of Production Example 1. The resin composition was as follows: phthalic anhydride 133.2 parts (0.9 mol), trimethylolpropane 136 parts (1.0 mol), coconut oil fatty acid 105 parts (0.5 mol). The resin solution had a solid component concentration of 60.3%, a varnish viscosity of P, a resin acid value of 7.0, and a resin hydroxyl value of 105. The varnish solvent is xylol/isobutanol=60/40.

### Production Example 24

#### Production of acrylic resin solution X

An acrylic resin solution X having the following composition was prepared using azobisisobutyronitrile as a condensation catalyst. The acrylic resin solution X had a solid component concentration of 50.0%, a varnish viscosity of T (Gardner viscosity, 25°C), and a resin acid value of 15.4. The varnish solvent is xylol/n-butanol=80/20.

#### Composition of acrylic resin solution X

styrene	30 parts
n-butyl methacrylate	30 parts
n-butyl acrylate	20 parts
2-hydroxyethyl methacrylate	18 parts
acrylic acid	2 parts

#### [Preparation of painting substrate]

A polybutadiene electrodeposition paint is applied by using an electrodeposition coating method onto a door part of an automobile body, which has been subjected to a zinc phosphate treatment so that the thickness of the film after being dried is 20  $\mu$ , and baked at 170°C for 20 minutes. Then, the application surface is polished with a #400 sandpaper, and then the surface is wiped off using a gauze dampened with petroleum benzin, thereby degreasing the sur-

face. Thereafter, an amino-alkyd resin intermediate paint for automobiles is applied so that the thickness of the film after being dried is 25  $\mu$ , and baked at 140°C for 30 min. Then, the application surface is wet-sanded with a #400 sandpaper, drained/dried, and the application surface is wiped off using petroleum benzin, thereby obtaining the painted substrates of the examples of the present invention and those of the comparative examples.

#### Example 1

Using the silicone-modified polyester resin solution K obtained in Production Example 11 above, a maroon color topcoat paint having the following composition was produced by ball mill dispersion.

60% silicone-modified polyester resin solution K		117 parts
60% Yuban 28SE	(see Note 1)	50 parts
Perindo Maroon R-6422	(see Note 2)	10 parts
Toda Color KN-0	(see Note 3)	1 parts
NeO Spectra Beads AG	(see Note 4)	0.3 part
(Note 1) a melamine resin manufactured by Mitsui Toatsu Kagaku		
(Note 2) Maroon organic pigment manufactured by Bayer (Germany)		
(Note 3) Iron Oxide Red manufactured by Toda Kogyo		
(Note 4) Carbon black manufactured by Columbia Carbon (U.S.)		

0.05 PHR of Modaflow (manufactured by Monsanto) and 0.01 PHR of silicone oil KP-323 (manufactured by Shinetsu Kagakusha) were added to the paint as an application surface conditioner.

The obtained paints were diluted to a viscosity of 25 sec (Ford cup No. 4, 20°C) by using a mixed solvent of Sukuzol #1500/xylol/butyl acetate/n-butanol=30/20/30/20.

The diluted paint was air-sprayed on a painting substrate prepared in advance so that the thickness of the film after being dried is 30  $\mu$ , and left standing at room temperature for 10 min. Then, the sprayed paint was baked for 30 min at a temperature of 140°C by using an electric hot air dryer. The test results for the resultant painted plate are shown in Table 4.

#### Examples 2-12, Comparative Example 1-7

Using each of the silicone-modified polyesters obtained in the production examples above, a paint was produced in a manner similar to that of Example 1 based on the paint composition shown in Table 3. The produced paint was applied on a painting substrate.

The test results are shown in Table 4.

Table 3

No.	Composition
Example 2	60% silicone-modified polyester 117 parts
	resin solution K
	60% Yuban 28SE 50
	Titanium White JR-602 40
	(Manufactured by Teikoku Kako)
Example 3	60% silicone-modified polyester 117 parts
	resin solution L
	60% Yuban 28SE 50
	phthalocyanine green GBN 15
	(Manufactured by ICI (U.K.), Green organic pigment)
	Toda Color KN-0 3
Example 4	NeO Spectra Beads AG 0.2
	60% silicone-modified polyester 125 parts
	resin solution M
	60% Yuban 28SE 42
	Cyanin Blue-5023A 8
	(pigment manufactured by Dainippon Ink Kagaku Kogyo)



	Titanium White JR-602	5
Example 5	60% silicone-modified polyester resin solution M	117 parts
	60% Yuban 28SE	42
	Takenate B-815N	8.3
	(Manufactured by Takeda Chemical Industries, Co., Ltd., block type polyisocyanate, -solid component: 60%)	
	Formate TK-1	0.1
	(Manufactured by Takeda Chemical Industries, Co., Ltd., dissociation catalyst for block type polyisocyanate)	
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Example 6	60% silicone-modified polyester resin solution N	117 parts
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Example 7	60% silicone-modified polyester resin solution O	117 parts
	60% Yuban 28SE	42
	ADDITOL VXL-80	5
	(manufactured by Hoechst Japan Ltd., block type polyisocyanate)	
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Example 8	60% silicone-modified polyester resin solution O	117 parts
	60% Yuban 28SE	42
	ADDITOL VXL-80	5
	phthalocyanine green GBN	15
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Example 9	60% silicone-modified polyester	108 parts

	resin solution P	
	60% Yuban 28SE	50
	Takenate B-815N	8.3
	Formate TK-1	0.1
	Cyanin Blue 5023A	8
	Titanium White JR-602	5
Example 10	60% silicone-modified polyester	117 parts
	resin solution U	
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Example 11	60% silicone-modified polyester	117 parts
	resin solution V	
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Example 12	60% silicone-modified polyester	117 parts
	resin solution Q	
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Comparative Example 1	60% polyester resin solution A	117 parts
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Comparative Example 2	60% silicone-modified polyester	117 parts
	resin solution R	
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Comparative	60% silicone-modified polyester	117 parts

Example 3	resin solution S	
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Comparative Example 4	60% silicone-modified polyester	117 parts
	resin solution T	
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
Comparative Example 5	NeO Spectra Beads AG	0.3
	60% alkyd resin solution W	117 parts
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
Comparative Example 6	NeO Spectra Beads AG	0.3
	60% alkyd resin solution W	117 parts
	60% Yuban 28SE	42
	Takenate B-815N	8.3
	Formate TK-1	0.1
Comparative Example 7	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
	50% acrylic resin solution L	140 parts
	60% Yuban 28SE	50

Table 4

Performance of applied film	Example	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
finish appearance (gloss, the thick touch, etc.). (see Note 1)		◎	◎	○	◎	◎	◎	◎	◎
60° mirror reflectance		93	97	92	96	98	98	97	97
pencil hardness		F	H	H	F	F	H	H	H
shock resistance (cm) (Du Pond measurement, $\varphi = 1/2"$ , 500g)		40	30	35	40	40	30	35	35
Erichsen value (mm)		42	37	42	47	50	32	40	39
gasoline wiping resistance (see Note 2)		good	good	good	good	good	good	good	good
acid resistance (see Note 3)		normal	normal	normal	normal	normal	normal	normal	normal
Waxing resistance (before exposure) (see Note 4)		◎	◎	○	○	○	○	◎	○
Waxing resistance (sunshine weatherometer, after 400 hours) (see Note 4)		○	○	○	○	○	○	○	○
weather resistance (sunshine weatherometer, gloss retention after 800 hours) %		90	93	91	91	92	91	93	89
interlayer adhesion (see Note 5)		○	○	○	○	○	○	○	○
dust repelling resistance (see Note 6)		○	○	○	○	○	○	○	○
Bubbling critical thickness, $\mu$ (see Note 7)		> 50	> 50	> 50	> 50	> 50	> 50	> 50	> 50
Running critical thickness, $\mu$ (see Note 8)		> 50	> 50	> 50	50	50	> 50	> 50	> 50

Table 4 (continued)

Example 9	Example 10	Example 11	Example 12	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7
☉	○	☉	○	○	○	△ insufficient gloss	X no gloss	○	○	△ insufficient thick touch
96	92	95	90	91	95	84	70	94	95	94
F	F	F	HB	F	B	H	8H	F	F	F
30	40	40	40	40	40	30	35	25	30	20
37	43	40	45	45	50	34	0.9	40	42	30
good	good	good	good	good	gloss buried	good	good	good	good	substantial scratch
normal	normal	normal	normal	normal	discoloring, blistering	normal	normal	normal	normal	normal
☉	☉	○	○	☉	△	○	○	X	X	△
○	○	○	△	○	X	☉	○	X	X	X
90	90	89	85	80	70	90	80	82	72	85
○	○	○	○	○	○	○	○	X	X	X
○	○	○	○	△	○	☉	△	○	○	○
>50	>50	>50	>50	35	>50	>50	44	50	50	38
50	50	>50	>50	40	40	>50	>50	50	50	35

(Note 1) The finish appearance was evaluated in terms of the thick touch based on the following criteria.

- ◎: Very good
- : Good
- △: Fair
- △: Poor
- ×: Very poor

(Note 2) Gasoline wiping resistance: A gauze was dampened with Nisseki Silver Gasoline, and the application surface was strongly rubbed with the gauze over a length of 10 cm for 8 reciprocations, after which the application surface was observed. Those having substantially no scratch or gloss blurring on the application surface were considered as "good".

(Note 3) Acid resistance: 0.5 cc of 10% sulfuric acid was dropped onto the application surface, and left standing at 20°C, 75 %RH for 48 hours. Then, the application surface was washed with water, and observed.

(Note 4) Waxing resistance: A small amount of a car wax "Soft 99 Hanneri" (manufactured by Nitto Kagaku) was applied on a piece of white flannel cloth, and the application surface was strongly rubbed with the cloth by using the index finger over a length of 10 cm for 10 reciprocations. Thereafter, the wax remaining on the application surface was removed with a new piece of flannel cloth, and then the application surface was observed. The gloss burring and scratch on the application surface and the degree of coloring of the white flannel cloth were comprehensively evaluated based on the following criteria.

◎: No gloss burring or scratch on application surface and no coloring of flannel cloth

○: Substantially no gloss burring or scratch on application surface and substantially no coloring of flannel cloth

○<sup>-</sup>: Slightly poorer than ○ but better than ⊕

⊕: Slight gloss burring and/or scratch on application surface and slight coloring of flannel cloth observed (threshold for practical use)

△: Considerable gloss burring and/or scratch on application surface and considerable coloring of flannel cloth

×: Significant gloss burring and/or scratch on application surface and significant coloring of flannel cloth

(Note 5) The painted plates produced in the examples and the comparative examples are further over-baked at 160°C for 90 min, and then the respective topcoat paints are sprayed and baked at 120°C for 30 min (Each topcoat paint is over-coated with the same topcoat paint). Thereafter, the application surface is scratched with a cross cut using a razor, and a peeling test is performed with a cellophane tape. The over-coated films which do not peel from each other are marked with ○, and those which peel from each other are marked with ×.

(Note 6) Dust repelling resistance: Paints used in the examples and the comparative examples are air-sprayed onto a painting substrate, and left standing at room temperature for 3 min. Thereafter, an amino-alkyd resin topcoat paint for automobiles in the form of mist is sprayed onto the painting substrate. After standing for 10 min, the paint is baked at 140°C for 30 min, and the state of the mist paint on the application surface was evaluated.

○: Paint is cured while remaining the form of fine mist as applied. The application surface appears normal.

⊕: Mist pattern is spread.

△: Mist portion is indented.

X: Mist paint is spread and repelled all over the application surface.

(Note 7) Bubbling critical thickness: Each of the paints used in the examples and the comparative examples is applied at a discharge rate of 200 cc/min onto a horizontal painting substrate with a thickness gradient such that the thickness of the film after being dried gradually increases from the left-hand side of the painted plate to the right-hand side thereof, and left standing at room temperature for 10 min. Thereafter, the applied paint is baked at a temperature of 140°C for 30 min by using an electric hot air dryer. The thickness of the location of the application surface at which a significant level of bubbling starts to appear is measured as the bubbling critical thickness.

(Note 8) Running critical thickness: Each of the paints used in the examples and the comparative examples is applied in a manner as described in (Note 7) onto an inclined painting substrate with a thickness gradient. The painting substrate is provided with holes having a diameter of 6-8 mm in advance. After the application, the applied paint is left standing for 10 min with the painting substrate being inclined, and baked at a temperature 140°C for 30 min by using an electric hot air dryer. The inclination angle of the painting substrate needs to be kept at 60° or more with respect to the horizontal plane until the end of the evaluation. After drying, the thickness of the location of the application surface around the hole portion at which running starts to appear is measured as the running critical thickness.

Examples 1-12 are silicone polyester topcoat paint compositions of the present invention, and each of them exhibits a good property in each test. Comparative Example 1 is a case where an unmodified oil-free polyester is used,



and is slightly poorer in terms of the application property, e.g., the dust repelling resistance, the bubbling critical thickness and the running critical thickness, as compared to a silicone-modified polyester. Comparative Example 2 uses an oil-free polyester resin whose hydroxyl value is less than 60. Therefore, the curing is insufficient, whereby the paint is inferior in terms of the hardness, the gasoline wiping resistance, the shock resistance, the waxing resistance, etc. Comparative Example 3 is a case where the content of the aromatic polybasic acid (isophthalic acid) in the polybasic acid component of an oil-free polyester resin is over 55 mol%. Comparative Example 3 has deficiencies in the appearance of the application surface, e.g., insufficient gloss, and insufficient luster, due to the poor compatibility with the amino-aldehyde resin. Comparative Example 4 is an example where an oil-free polyester resin whose hydroxyl value is 200 or more is modified with a silicone, and has deficiencies as those in Comparative Example 3. Comparative Example 4 is also inferior in terms of the dust repelling resistance, the bubbling critical thickness, etc. This appears to be because of the insufficient pigment dispersibility, the insufficient compatibility, the surface hardening (skinning), etc., which are due to the high polarity of the resin. Each of Comparative Examples 5 and 6 is an example where an alkyd resin is used, and inferior in terms of the waxing resistance before and after exposure, the interlayer adhesion, and the gloss retention in the promoted weather resistance test. Comparative Example 7 is an example where an acrylic resin is used, and the thick touch on the application surface is insufficient. Comparative Example 7 is inferior in terms of the waxing resistance, the interlayer adhesion, the bubbling critical thickness, the running critical thickness, etc. It is evident from the above that the silicone-modified polyester topcoat paint composition of the present invention has a very desirable performance.

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④ シリコン変性ポリエステル系上塗り塗料組成物

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明 細 書

## 1. 発明の名称

シリコン変性ポリエステル系上塗り塗料組成物

## 2. 特許請求の範囲

1. (A) シリコン変性ポリエステルと (B) アミノアルデヒド樹脂及び/又はブロンタイソシアネートからなるバインダー成分及び (C) 顔料を必須成分として含有するシリコン変性ポリエステル系上塗り塗料組成物において、成分 (A) はそのポリエステルを形成する酸成分の少なくとも25モル%が飽和脂族多価基であり、かつ水酸価が60~200のオイルフリー飽和ポリエステル樹脂15~97重量部を分子量約500~約2000の反応性オルガノポリシロキサン樹脂3~25重量部で変性したものであり、成分 (A) と成分 (B) の含有割合は (A) の60~

80重量部に対し、(B) 10~40重量部であり、そして顔料の含有量は3~100 PBRであることを特徴とするシリコン変性ポリエステル系上塗り塗料組成物。

2. ポリエステルを形成する酸成分が飽和脂族多価基の他に、芳香族多価基及び一置式  $\text{HOOC}(\text{C}_6\text{H}_4)_n\text{COOH}$  (式中  $n$  は1~12の整数) で換えられる直鎖状飽和二価基からなる群の少なくとも1種からなる特許請求の範囲第1項記載の組成物。

3. 飽和脂族多価基と芳香族多価基の合計が70モル%以上かつ芳香族多価基の含有量が55モル%以下である特許請求の範囲第2項記載の組成物。

## 3. 発明の詳述な説明

本発明はシリコン変性ポリエステル/アミノアルデヒド樹脂及び/又はブロンタイソシアネー

ト系の吹付け用紙用上塗り塗料組成物に関するものである。

従来、自動車車体等の上塗り塗料としては、アミノアルキド樹脂系、アミノアクリル樹脂系、アクリルラッカー系などの塗料が用いられている。アミノアルキド樹脂系塗料は乾燥のし易さや、仕上り外観（塗装のツヤ、肉持感をと）、塗料組成物の高い組成での耐候性（光沢保持性）がすぐれているなどの特徴を有しているが、塗料組成物が（かつ塗料中に白色以外の着色顔料（以後着色顔料という）を多く含むいわゆる顔料系系の塗料では、ワックスがけしたとき塗面にスリキズやツヤボケが生じ、かつワックスが着く着色する等の、耐ワックスがけ性に劣る点が問題となっていた。この耐ワックスがけ性は塗膜厚の厚みにも、また塗料組成物の組成にも要求される性能であるがアミノアルキド樹脂系上塗り塗料ではこれを満

を有しながら、乾燥のし易さ（ハジキが発生しないことなど）、面状塗面がいわゆるボケたような感じとなりツヤ感が劣ること、アミノ樹脂との相溶性が悪いことなどの点により、特に自動車車体の上塗りには適用困難とされていた。

特異な組成のオイルフリーポリエステル樹脂を用いることにより、塗膜のツヤ感、ハジキ抵抗性、アミノアルキド樹脂との相溶性及び乾燥のし易さ（乾燥性）等の改善されたオイルフリーポリエステル／アミノアルキド樹脂系上塗り塗料が提案された（特開昭56-157481号）。

本発明の目的は、オイルフリーポリエステルの長所を保ちつつ、乾燥性、塗膜のツヤ感、ハジキ抵抗性など、特に塗膜性が、上記従来の塗料よりもさらに一層向上した上塗り塗料組成物を提供することにある。

上記本発明の目的は、(A)シリコーン変性ポ

特開昭56-157481(2)

足させることは困難である。アミノアクリル樹脂系上塗り塗料は塗料組成物の低い組成（40～80 PPR以下）での耐候性はかなりすぐれているが、塗膜の耐ワックスがけ性は必ずしも良好でない。特に自動車車体の上塗り用として要求される性能すなわち、ノンサンド層間付着性（一度塗付た塗膜の上に補修塗りのため同じ塗料をもう一度塗装し、焼き付け場合の塗膜間の付着性）、エリクセン試験、耐腐蝕性、および仕上り外観（ツヤ、肉持感）等の要求を満足させることが困難である。アクリルラッカー系は乾燥時間短縮分濃度が著しく低く、塗装工程数を多くしなければならぬ欠点がある。

前記塗料に対しオイルフリーポリエステル／アミノアルキド樹脂系塗料は、耐候性、塗膜の機械的性質（エリクセン試験、耐腐蝕性）層間付着性、乾燥時の塗料分濃度の高いこと、などの特徴

リエステルと(A)アミノアルキド樹脂及び／又はブロンクイソシアネートからなるバインダー成分及び(C)顔料を必要成分として含有するシリコーン変性ポリエステル系上塗り塗料組成物において、成分(A)は、そのポリエステルを形成する酸成分の少なくとも33重量%が飽和環状多環基であり、かつ水酸基価が60～300のオイルフリー飽和ポリエステル樹脂73～97重量部を分子量約500～約2000の反応性オルガノポリシロキサン樹脂3～23重量部で変性したものであり、成分(A)と成分(B)の含有割合は(A)の60～90重量部に対し、(B)10～40重量部であり、そして顔料の含有量は1～100 PPRであることを特徴とする本発明のシリコーン変性ポリエステル系上塗り塗料組成物によつて達成される。

本発明の塗料組成物の優れた乾燥性は、塗膜の

断に発生するブレとワキの、好ましくない現象を  
高水準でバランスよく抑制した点に、主として  
由来する。

一般に「ブレ」とは、例えばスプレー塗膜によ  
つて塗料を塗面に塗かれた被塗物に塗膜する場合、  
塗着した塗料が重力によつて被塗物上で流れ落ち  
る現象をいう。被塗物に塗着された塗料はブレの  
現象を生じることなく、塗着した場所に留まつて  
いることが必要であり、さもなければ、著しく膜  
厚が不均一となり、あるいは塗面に流れ落ちが生  
生して良好な塗膜を得ることができない。

上記ブレの現象は塗膜の膜厚が一定厚さ以上  
厚くなると急に発生するものであつて、このブレ  
が急に発生するようになる膜厚を「ブレ限界膜厚」  
と称している。ブレ限界膜厚は大きいほど塗着性  
の良好な、すなわち塗りぬき塗料といふことがで  
きる。

の粘着上料を減らし、その結果流れぬくして、ブ  
レ限界膜厚を低くしてしまう。

オイルフリーポリエステルは、一般にアルキド  
樹脂やアクリル樹脂と比較して、前記したブレと  
ワキの両者のバランスのとれた良好なレベルを保  
つことが難しいものであるが、本発明に従い特定  
のオイルフリーポリエステルを少量のシリコン樹  
脂で変性するならば、次のとおり、ワキ及び  
ブレを非常に高いレベルでバランスさせ得ること  
が見い出された。

従来にもシリコン変性ポリエステルあるいは  
シリコン変性アルキド樹脂は、プレコートメ  
ル用塗料に使用されていた（特開昭47-214  
02号公報など）が、従来の、これらのシリコ  
ン変性樹脂は30重量%以上に及ぶ量のシリコ  
ン樹脂を含有せしめ、それによつて耐腐蝕塗料  
の耐腐蝕性及び耐熱性を改善せしめようとするもの

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「ワキ」とは乾付型塗料において、乾付後から  
でてきた塗膜表面上に気泡の抜け残や、気泡そ  
のものの形が発生している現象を云う。ワキの原  
因は乾付時に塗料中の溶剤が急激に蒸発したり、  
塗膜時にまきこまれた空気の泡の抜けによつて生  
ずるといわれ、この現象も塗膜の厚さがある一  
定厚さ以上になると急に発生する。この膜厚を  
「ワキ限界膜厚」と称し、その値が大きい程塗着  
性が良好である。

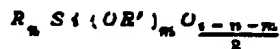
上記のようにブレ限界膜厚及びワキ限界膜厚が  
ともに大きい塗料が塗着し易い塗料であるが、こ  
の両者は一般に相反する傾向を持ち、両立させる  
ことが困難な場合が多い。すなわち一方を大にす  
ると他方は小となつてしまい、両方が大である塗  
料を得ることは難しい。たとえばワキ限界膜厚を  
大にするためには沸点の高い溶剤もしくは低い揮  
発性を多用すればよいが、そのことは塗着した塗料

であつた。

これに対し、本発明においては少量のシリコ  
ン樹脂で特定のポリエステルを変性することによ  
り実用上塗料の塗着性を著しく改善したもの  
である。

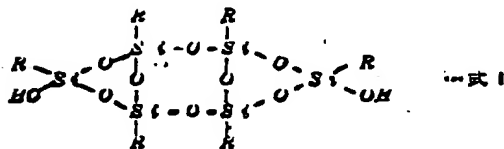
本発明において用いられるシリコン変性ポリ  
エステルの基体樹脂となるオイルフリーポリエス  
テルは、全炭素成分の少なくとも25モル%、好ま  
しくは少なくとも40モル%の飽和脂環族多塩基  
酸(1)を含有する点で特徴的である。該ポリエ  
ステルの炭素分、すなわち多塩基酸原料の残りは  
芳香族多塩基酸(2)及び/又は一般式  
 $\text{HOOC}(\text{C}_6\text{H}_4)_n\text{COOH}$  (nは1~12の整数)で  
示される直鎖状脂肪二塩基酸(3)であることが  
できる。さらに、好適な基体ポリエステルを調製  
するには、上記成分(1)と(2)の多塩基酸成  
分の合計量が70モル%以上で、かつ成分(1)

ガノポリシロキサン樹脂である。



ここでRは炭素-ケイ素結合によりケイ素に結合する一価有機基、R'は水素、C<sub>1</sub>~C<sub>10</sub>のアルキル基又はアリール基を示す。上式中のn及びmはそれぞれ4以下の値で、かつn+mは4以下でなければならない。

本発明で使用するシリコーン樹脂は、上式中(OR')で示される有機基、アルコキシ基のようを反応性基を分子中に2個以上有することが望ましい。このようなシリコーン樹脂としては、例えばS-8018(Dow Corning社製品、分子量1600、式1によつて表わされるRの定義)



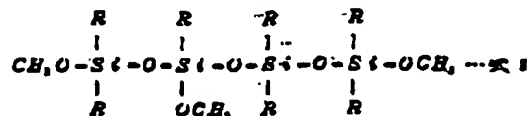
エステルとシリコーン樹脂の含有割合で基体ポリエステルの87~95重量部に対してシリコーン樹脂3~25重量部、好ましくは93~88重量部に対して7~13重量部であり、シリコーン樹脂が8重量部以下ではシリコーン変性ポリエステルの特長であるべき原料分散性が低下してしまい、添加のボケ料の不具合が発生し、また、加熱時にヘジキが頻発しおきる時製造操作性の低下が起る。一方、25重量部以上では樹脂コストが高くなり、耐アルカリ性の低下及び酸化性の低下が生じ上塗り塗料としての適性を失なうようになる。


本発明で用いられるシリコーン変性ポリエステルは、基体ポリエステルとシリコーン樹脂を上記した使用割合で、それぞれ公知の手段で混合させることによつて製造することができる。その反応条件としては溶剤の存在下あるいは不溶媒下で80℃以下、好ましくは150℃以下に加熱す

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[R: -CH<sub>3</sub>、又は  を表す]

やZ-5188(Dow Corning社製品、分子量660、式2によつて表わされるRの定義)



[R: -CH<sub>3</sub>、又は  を表す]

をはじめ、Sylkyd 50、DC-8037(Dow Corning社製品)、KR-216、KR-218、KSP-1(信越シリコーン(株)製品)、TSR-180、TSR-168(東京エレクトロ(株)製品)、SH5050、SH6018、SH6188(東レシリコーン(株)製品)等が挙げられる。

本発明において基体ポリエステルをシリコーン樹脂で変性してシリコーン変性ポリエステルを製造することによりシリコーン樹脂の使用量は基体ポリ

エステルに比べて減少する。使用される溶剤としては、芳香族系、エステル系、ケトン系、石油系など通常原料に使用される溶剤が沸点と共重合反応温度との関係を考慮して使用される。アルコール系溶剤は共重合反応を遅くするので好ましくない。また上記共重合反応を促進する為に触媒を使用することが望ましい。使用される触媒剤としてはオクタン酸、オクタン酸塩、水酸化カリウム、カトレンスルホン酸、オクタン酸第1スズ、テトラアルキルチタネート、塩酸、リン酸、高級脂肪酸無水マレイン酸等が用いられる。

本発明は、上記した如く特定のポリエステルを少量のシリコーン樹脂(3~25重量部)で変性して得られるシリコーン変性ポリエステルを上塗り塗料用樹脂として使用することによつて塗膜性を顕著に改善したものである。この塗膜性とは、塗膜の加熱硬化時のワキ、シレ性、弾性を上げる

こと及び加熱硬化時の半硬化状態に異種アミノ酸（アミノアルキド樹脂系塗料、アミノアクリル樹脂系塗料等）がかかつた際のヘジキ、ヘコキを防止すること等を指す。又シリコーン樹脂により、かかる利点に付随して、塗料の分散性が上昇することや、相溶性、溶剤に対する溶解性が上昇し、このためにスプレー塗布時の図形再現性が高くなる等の利点があり、さらにまた、形成される塗膜の光沢、耐水性も従来のオイルフリーポリエステル系上塗り塗料より格段に優れている。上記のような特長は、本発明に示した特定組成のポリエステルを、 $8 \sim 25$ 重量部の範囲でシリコーン樹脂化した樹脂を使用することにより初めて達成されるものであり、特に自動車用上塗り塗料として使われたものである。本発明に特定した以外の組成のポリエステルをシリコーン樹脂化しても、塗膜性能改善の効果は少なく、自動車用上塗り塗料としての実

（株）製品）、タケネート B-840N（東田製品（株）製品）、Address 1085（Yoda Chemicals 社（株））、ADDITOL VXL-80（ヘキストジャパン（株）製品）などがある。これらのブロック型ポリイソシアネートを使用する際には必要に応じてブロック型の触媒を促す触媒を添加して用いてもよい。

上記のアミノアルデヒド樹脂及びブロック型ポリイソシアネートはそれぞれ単独で利用してもよく、また両者を併用してもよい。

本発明の塗料組成物中のバインダー成分組成はシリコーン樹脂化ポリエステル／アミノアルデヒド樹脂及び／又はブロック型ポリイソシアネートの重量比が  $90/10 \sim 10/90$  の範囲にある必要がある。触媒剤であるアミノアルデヒド樹脂及び／又はブロック型ポリイソシアネートがこの組成物に、耐水性、耐塩性、耐汚染性等が低下し、固より少ないと硬化不足となり、VOC の範囲より過

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用途が得られない。

本発明において触媒剤成分（B）として用いるアミノアルデヒド樹脂は、アミノ基分としてメラミン、尿素、ベンゾジアミン、アセトジアミン、スチロジアミン、スビロジアミン等があげられ、通常塗料に用いられる殆んどのアミノアルデヒド樹脂が使用できる。なかでも最も好ましいものは耐水性の面からメラミンホルムアルデヒド樹脂である。これらのアミノアルデヒド樹脂には硬化温度を下げるために常用の硬化触媒を添加することもできる。

また、ブロック型ポリイソシアネートは、無官能型ポリイソシアネートを例えば脂肪族又は芳香族モノアルコール、フェノール、エキシム、カプロラクタムのような常用のブロック剤を用いてブロック型ポリイソシアネートにしたものであり、たとえば、タケネート B-815N（東田製品

製品）が多いと、塗膜がもろくなつてしまふ。

本発明の塗料組成物における塗料濃度は  $100 \text{ PFR}$  以下であればよいが、通常の自動車車体等の上塗り用塗膜の厚さ（約  $20 \sim 50 \mu$ ）で下地を完全に隠蔽するには一般に  $2 \text{ PFR}$  以上が必要である。 $100 \text{ PFR}$  以上では耐水性が、アミノアルキド樹脂系上塗り塗料と同程度となり発明の利点が少なくなつてくる。

本発明の塗料組成物では曝露面及び過渡性の耐ワックスがけ性、特に着色塗料を多く含む塗色の場合の耐ワックスがけ性が非常にすぐれており、塗料成分中着色顔料／チタン白顔料の重量比が  $100/0 \sim 20/80$ 、好ましくは  $100/0 \sim 60/40$  の範囲にあると本発明の効果が特に顕著である。

本発明の塗料組成物を用いて自動車車体を塗装するには、まずシリコーン樹脂化ポリエステル成分

(A)および無機物成分(B)からなるバインダー成分に通常用いられる着色顔料、必要ならば添加剤などを配合して通常の方法で塗料を作り、このものを塗布用材料により塗料粘度がフオードカソプA(30℃)で20~30秒に調整する。ついで、これを下塗りおよび必要に応じて中塗り塗膜を形成せしめた基材表面上に乾燥塗膜が約20~60μmなるように塗布する。塗布方法は通常のエアスプレー、エアレススプレー、静電塗布などで行なう。つぎに数分間常温下で放置後50~160℃で20~40分間加熱せしめて上塗り塗膜が得られる。

本発明のシリコン又はポリエステル系上塗り塗料組成物は、自動車の上塗り用として要求される諸条件のうち、塗着性、顔料分散性、塗膜外観、塗膜の機械的性質、耐薬品性、耐熱性などは自動車の上塗り用として最も多く用いられているア

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ミノアルキド樹脂系塗料と同程度の性能を有し、アミノアルキド樹脂系塗料の欠点である、低顔料濃度領域での耐熱性(光沢保持性)、塗膜前及び塗膜後の耐ワックス掛け性においてはアミノアルキド樹脂系よりはるかにすぐれている。また、層間付着性においてもアミノアルキド樹脂系塗料よりすぐれている。さらに、アミノアルキド樹脂系塗料と比較して、耐熱性(光沢保持性)、層間付着性、塗膜の機械的性質などが非常にすぐれており、特に、着色顔料を多く含むダークグリーン、ダークマールン、ダークブルーなどの彩度の高い着色の塗膜での塗膜前及び塗膜後の耐ワックス掛け性がすぐれている。

以上に述べたように本発明の塗料組成物は塗着性、耐熱性及び顔料分散性が著しく優れているので自動車車体のみならず建築のツヤ、肉持ち漆および耐熱性を必要とする家電用その他の一般工業

用塗料として広く使用することができる。

以下実施例によつて本発明をより詳細に説明する。実施例中の部及び多は特にことわらない限り重量部及び重量を示す。

#### 実施例 1

##### オイルフリーポリエステル樹脂組成物Aの製造

加熱装置、攪拌器、真空装置、水分脱除、精製塔及び計量計を備えた反応槽に、ヘキサヒドロ無水フタル酸5.9部(0.35モル)、イソフタル酸3.81部(0.35モル)、アジピン酸2.82部(0.2モル)、トリメチロールプロパン4.08部(0.3モル)およびネオペンタグリコール7.25部(0.7モル)を仕込み加熱する。原料が融解し、成分が均一となつた後槽を冷却し、反応槽温度を230℃に冷却させる。ただし160℃から230℃までは3時間かけて均一温度で昇

温させ、生成する縮合水は系外へ除去する。

230℃に達したら、そのとき温度を一定に保ち2時間後槽を冷却する。その後、反応槽内にキノールを添加し、溶剤存在下の縮合に切り替え、反応を続ける。温度7℃に達したら反応を終了し冷却する。冷却後スワゾール41500(丸管石油化学(株)製品)100.8部、セロソルブアセテート45.1部を加えて、オイルフリーポリエステル樹脂Aを製造した。オイルフリーポリエステル樹脂Aの固形分濃度は62.0%、ワニス粘度(ガードナー粘度、25℃)はV、樹脂の価値は7.0及び水酸価値182であつた。

#### 実施例 2~10

オイルフリーポリエステル樹脂組成物B~Jの製造  
表-1に示す原料成分を用い、オイルフリーポリエステル樹脂組成物B~Jを、製造例1と同様な方法で製造した。それらのワニス粘度値を表-1

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表 - 2

記 号	L	M	N	U	P	Q	R	S	T	U	V
ポリエステル樹脂溶液名	B	C	D	E	F	G	H	I	J	A	A
同配合量	150g	150g	150g	140g	140g	150g	140g	150g	150g	150g	150g
シリコン中間体名	SH 6155	DC- 3037	SH 6155	SH 6155	DC- 3037	SH 6155	SH 6155	SH 6155	SH 6155	SH 6155	SH 6155
同配合量	11g	11g	11g	11g	11g	11g	11g	11g	11g	11g	11g
固形分濃度(%)	60.2	60.2	60.1	60.2	60.2	60.2	60.2	60.1	60.2	60.2	60.2
ワニス粘度	WX	V	S	S, S,	T	2Z,	U	S,	P	X	YF
シリコン実効量(%)	10	10	10	10	10	10	10	10	10	8	20

## 製 造 例 23

## アルキド樹脂溶液Wの製造

製造例1と同様の方法でアルキド樹脂溶液Wを製造した。樹脂組成は、無水フタル酸122.2部(0.5モル)、トリメチロールプロパン13.6部(2.0モル)、ヤシ油脂肪酸10.5部(0.5モル)であり、樹脂溶液の固形分濃度60.2%、ワニス粘度P、樹脂粘度7.0、樹脂水酸価105であった。ワニス溶剤はキシロール/イソブタノール=60/40である。

## 製 造 例 24

## アクリル樹脂溶液Zの製造

アゾビスイソブチロニトリルを重合触媒として下記の組成のアクリル樹脂溶液Zを調製した。アクリル樹脂溶液Zの固形分濃度は60.2%、ワニス粘度(ガードナー粘度、25℃)はT、樹脂粘度は1.54であった。ワニス溶剤はキシロール/

イソブタノール=60/40である。

## アクリル樹脂溶液Zの組成

ステレン	20部
α-ブチルメタクリレート	30部
α-ブチルアクリレート	30部
3-ヒドロキシエチルメタクリレート	10部
アクリル酸	2部

## 〔塗膜基材の準備〕

リン酸亜鉛処理済の自動車車体ドアペーンにポリブタジエン系電着塗料を電着塗膜法にて、乾燥膜厚が20μmとなるように塗膜し、140℃×30分焼きつける。ついでφ400サンデーパーペーにて塗面を研削した後、石油ベンゼンをしめらせたガーゼで塗面をふき加脂する。その後アノアルキド樹脂系自動車用中塗り塗料を、乾燥膜厚が25μmとなるように塗膜し140℃×30分焼きつける。ついでφ400サンデーパーペーで塗面



を水研し、水切り乾燥し、石油ベンジンで塵面を拭い、本発明の実施例および比較例用の塗膜面材とした。

#### 実施例 1

前記実施例 11 で得たシリコン変性ポリエステル樹脂溶液を用いて、ボールミル分散により下記配合でマールン色の上塗り用塗料を作成した。

60%シリコン変性ポリエステル樹脂溶液	117部
60%ニューバン 285E (注1)	50
ペリンドマルーン R-6422 (注2)	10
トダカラー KN-0 (注3)	1
Nee Spectra Beads AG (注4)	0.3

(注1) 三井東圧化学(株)製メフリン樹脂  
(注2) ベイエス社(独)製マールン系有機顔料  
(注3) 戸田工業(株)製、ベンガラ  
(注4) コロンビアカーボン社(米)製カーボンブラック

材上に塗膜した。

それぞれの試験結果を表-4に示す。

表 - 3

試料	配 合
実施例 2	60%シリコン変性ポリエステル樹脂溶液 117部
	60%ニューバン 285E 50
	タチン白 NR-602 (帝國化工(株)製品) 40
実施例 3	60%シリコン変性ポリエステル樹脂溶液 117
	60%ニューバン 285E 50
	フクロシアエングリーニング BN 12 (IC社(英)製、疎水性顔料)
	トダカラー KN-0 1
	Nee Spectra Beads AG 0.3

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塗料には塗膜調整剤としてゾフロ(マンテント(株)製品) 0.05 PHBとシリコンオイル SP-922 (信越化学社製品) 0.01 PHBを添加した。

得られた塗料をスプレーノズル 1500/キローノル/酢酸ブチル/エポキシノール=30/30/30/30の混合溶剤で粘度 25 秒(フォードカップ #4、25℃)に希釈した。希釈済み塗料を、筒もつて準備した塗膜基材上に、乾燥膜厚が 30μとなるようエアースプレーし、室温で 10 分間置いた後、電気熱風式乾燥機で 140℃の温度で 30 分間焼きつけた。得られた塗膜の試験結果を表-4に示す。

#### 実施例 2~12、比較例 1~7

前記実施例 1 に於いて得た各種シリコン変性ポリエステルを用い、表-3に示す塗料配合に基づき実施例 1 と同様の方法で塗料を作成し、塗膜材

実施例 4	60%シリコン変性ポリエステル樹脂溶液 117部
	60%ニューバン 285E 48
	シアニンプール-5023A (大日本インキ化学工業(株)製品) 0
実施例 5	タチン白 NR-602 5
	60%シリコン変性ポリエステル樹脂溶液 117
	60%ニューバン 285E 48
	タチネート R-615N (東田薬品(株)製、フロンク型ポリイソシアネート、固形分 60%) 0.3
	フォーノート TK-1 (東田薬品(株)製、フロンク型イソシアネートの誘導体) 0.1
	ペリンドマルーン R-6422 10
	トダカラー KN-0 1
	Nee Spectra Beads AG 0.3

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実施例 6	60%シリコン交性ポリエス テル樹脂組成物N	117部
	60%ムーベン28SE	50
	ペリンドマルーンR-6422	10
	トゲカラ-KN-0	1
	Neo Spectra Beads AG	0.3
実施例 7	60%シリコン交性ポリエス テル樹脂組成物U	117
	60%ムーベン28SE	42
	ADDITOL VXL-80 (ヘヤストジヤベン社製、ブロン ク型ポリイソシアネート)	5
	ペリンドマルーンR-6422	10
	トゲカラ-KN-0	1
	Neo Spectra Beads AG	0.3

実施例 8	60%シリコン交性ポリエス テル樹脂組成物U	117部
	60%ムーベン28SE	42
	ADDITOL VXL-80	5
	フロンティアエンダリーングBN	15
	トゲカラ-KN-0	1
	Neo Spectra Beads AG	0.3
実施例 9	60%シリコン交性ポリエス テル樹脂組成物P	102
	60%ムーベン28SE	50
	ダケネートB-818N	1.23
	フォーメートTE-1	0.1
	シアニンプル-5023A	8
	チタン酸JR-802	5

実施例 10	60%シリコン交性ポリエス テル樹脂組成物U	117部
	60%ムーベン28SE	50
	ペリンドマルーンR-6422	10
	トゲカラ-KN-0	1
	Neo Spectra Beads AG	0.3
実施例 11	60%シリコン交性ポリエス テル樹脂組成物V	117
	60%ムーベン28SE	50
	ペリンドマルーンR-6422	10
	トゲカラ-KN-0	1
	Neo Spectra Beads AG	0.3
実施例 12	60%シリコン交性ポリエス テル樹脂組成物Q	117
	60%ムーベン28SE	50
	ペリンドマルーンR-6422	10
	トゲカラ-KN-0	1
	Neo Spectra Beads AG	0.3

比較例 1	60%ポリエステル樹脂組成物A	117部
	60%ムーベン28SE	50
	ペリンドマルーンR-6422	10
	トゲカラ-KN-0	1
	Neo Spectra Beads AG	0.3
比較例 2	60%シリコン交性ポリエス テル樹脂組成物R	117
	60%ムーベン28SE	50
	ペリンドマルーンR-6422	10
	トゲカラ-KN-0	1
	Neo Spectra Beads AG	0.3
比較例 3	60%シリコン交性ポリエス テル樹脂組成物S	117
	60%ムーベン28SE	50
	ペリンドマルーンR-6422	10
	トゲカラ-KN-0	1
	Neo Spectra Beads	0.3

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比較例4	60%シリコーン実性ポリエス 117部 アル樹脂溶液T	
	60%エーバン28SE	50
	ペリンドマルーンR-6422	10
	トゲカラ-KN-0	1
	Nec Spectra Beads	0.3
比較例5	60%アクリド樹脂溶液W	117
	60%エーバン28SE	50
	ペリンドマルーンR-6422	10
	トゲカラ-KN-0	1
	Nec Spectra Beads AG	0.3

比較例6	60%アクリド樹脂溶液W	117部
	60%エーバン28SE	42
	アクリートB-518N	2.3
	フオーマーTK-1	0.1
	ペリンドマルーンR-6422	10
比較例7	トゲカラ-KN-0	1
	Nec Negative Beads AG	0.3
	60%アクリル樹脂溶液L	140
	60%エーバン28SE	50
	ペリンドマルーンR-6422	10
	トゲカラ-KN-0	1
	Nec Spectra Beads AG	0.3

表 - 4

性能項目	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	実施例7	実施例8
仕上り外観(ツヤ感、肉持ち感他)(注1)	◎	◎	◎	◎	◎	◎	◎	◎
60°鏡面反射率	92	97	92	96	93	93	97	97
鉛筆硬度	F	H	H	F	F	H	H	H
耐薬品性(%) (デュポン式、400F、500F)	40	30	35	40	40	30	35	35
エリヤセン値(mm)	42	27	42	47	20	22	40	20
耐カンリン耐水性(注2)	良好	良好	良好	良好	良好	良好	良好	良好
耐摩耗(注3)	異常なし	異常なし	異常なし	異常なし	異常なし	異常なし	異常なし	異常なし
耐ワックスがけ性(通電時)(注4)	◎	◎	○	○	○	○	◎	○
耐ワックスがけ性(ランシヤインロエゾノマー、400時間後)(注4)	○	○	○	○	○	○	○	○
耐薬性(ランシヤインロエゾノマー、500時間後の光沢保持率)、%	90	95	91	91	92	91	93	99
層間付着性(注5)	○	○	○	○	○	○	○	○
耐アルコール性(注6)	○	○	○	○	○	○	○	○
ワックス耐摩、μ(注7)	>50	>50	>50	>50	>50	>50	>50	>50
クレタ耐摩、μ(注8)	>50	>50	>50	30	30	>50	>50	>50

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表-4 図3

実施例8	実施例10	実施例11	実施例12	比較例1	比較例2	比較例3	比較例4	比較例5	比較例6	比較例7
○	○	◎	○	○	○	△ フヤ不足	× フヤなし	○	○	△ 両側面不足
30	32	33	30	31	33	34	30	34	33	34
F	F	F	HB	F	B	H	2H	F	F	F
30	40	40	40	40	40	30	35	35	30	30
27	43	40	45	43	30	24	33	40	43	29
良好	良好	良好	良好	良好	フヤボケ	良好	良好	良好	良好	スリ傷がかなりあり
異常なし	異常なし	異常なし	異常なし	異常なし	灰色、フタレ発生	異常なし	異常なし	異常なし	異常なし	異常なし
○	○	○	○	○	△	○	○	×	×	△
○	○	○	△	○	×	◎	○	×	×	×
30	30	33	35	30	30	30	30	33	33	35
○	○	○	○	○	○	○	○	×	×	×
○	○	○	○	△	○	◎	△	○	○	○
>30	>30	>30	>30	35	>30	>30	44	30	30	33
30	30	>30	>30	40	40	>30	>30	30	30	35

(注1) 仕上り外観をアナル、肉持感から次の基準で評価した。

◎：非常に良好

○：良好

◎：ほぼ良好

△：不良

×：非常に不良

(注2) 耐ガソリン拭拭性：日石ケルバーガソリンをガーゼにしめらせ、塗面の10mmの長さを強く8往復とすつた後塗面を観察した。ほとんどスリ傷、塗面のフヤボケの少ないものを良好とした。

(注3) 耐水性：105℃乾燥0.5hを塗面上に施下し20℃、75%RHで48時間放置した後水洗し塗面を観察した。

(注4) 耐ワックス附け性：自動車用ワックスSo/100ハネネリ(日東化学(株)製)を

を白いネルの布に少量つけて、人差し指で塗面を10mmの距離にわたって10往復、強くとする。その後、塗面に塗ったワックスを新しいネルの布でふきとり、塗面を観察する。塗面のフヤボケ、スリ傷と白いネル布への着色の着色の強度を総合的に次の基準で評価した。

◎：塗面のフヤボケ、スリ傷、ネル布の着色がない。

○：塗面のフヤボケ、スリ傷、ネル布の着色がほとんどない。

○：○よりやや劣るが◎より良好

◎：塗面にフヤボケ、スリ傷が少しありネル布への着色の着色もやや認められる。(実用上の境界)

△：塗面のフヤボケ、スリ傷がかなりあり、ネル布もかなり着色する。

X: 塗布のツヤボケ、スリ傷、キズ等の  
有無が著しい。

(注5) 各実施例、比較例で作製した塗膜をさら  
に160℃×60分オーバーベイトし、  
その後それぞれの上塗り塗料をスプレー  
塗布し、180℃×30分焼き付ける  
(同じ上塗り塗料どうしの塗り重ねとな  
る)。その後カミソリでクロスカット傷  
をつけ、セロハンテープで制膜試験を行  
なう。塗り重ねた塗膜間にヘガレを生じ  
ないものを○、ヘガレたものをXとした。

(注6) 耐グーストヘリヤ性: 各実施例及び比較例  
に用いた塗料を塗膜基材上にエアースプ  
レーした後、室温で3分間放置し、その  
後アミノアルキド樹脂系自動車用上塗り  
塗料のグーストをかける。10分間放置し  
た後140℃×30分焼き付け、塗面上

と同様に研削を行なう。塗膜表面には  
予じめ6~8mmの孔をあけておく。塗膜  
後、塗膜基材を植料させたまま10分間  
放置し、そのまま電気熱風式乾燥機で  
140℃の温度で30分間焼付けする。研  
削後の傾斜角は塗膜を水平面に対し、  
60度以上に保たねばならない。

乾燥後の孔下部にクレーが生じはじめる部  
位の膜厚を測定し、クレー膜厚とした。

実施例1~12は本発明のシリコーンポリエス  
テル系上塗り塗料組成物であり、それぞれの試験  
においてすぐれた特性を示している。比較例1は  
未変性オイルフリーポリエステルを用いた場合で、  
塗膜時の耐グースト抵抗性、ワキ、クレー膜厚等  
塗膜性は、シリコーン変性ポリエステルと比して  
やや劣る。比較例2はオイルフリーポリエステル  
の水酸価が60よりも低い樹脂を用いたため乾燥

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のグースト塗料の性状を評価した。

○: 細いグースト状で塗布した状態のまま  
硬化、塗面に異常はない。

◎: グーストが凝っている。

△: グースト部分が固みに凝っている。

X: 一面にヘリヤとなつて凝っている。

(注7) ワキ膜厚: 各実施例及び比較例に用  
いた塗料を水平な塗膜基材上に乾燥膜厚  
が塗板の左から右方向に徐々に厚くなる  
様にエアースプレーにより吐出量800cc  
/分で傾斜塗布を行ない、室温で10分  
間放置した後、電気熱風式乾燥機で  
140℃の温度で30分間焼き付ける。  
塗面に著しくワキが生じはじめる部位の  
膜厚を測定しワキ膜厚とした。

(注8) クレー膜厚: 各実施例及び比較例に用  
いた塗料を、傾斜した塗膜基材上に注

化不足となり硬度不足、耐カソリン抵抗性、耐酸  
性、耐ワックス耐性が劣っている。比較例  
3はオイルフリーポリエステル樹脂の多価基組成  
分の内の芳香族多価基(イソフタル酸)含有  
量が5重量%を上回った例であり、アミノアル  
キド樹脂との相溶性の悪さから、フヤ不足、充  
足不足等の塗面状態の欠陥がある。比較例4はオ  
イルフリーポリエステル樹脂の水酸価が200  
以上のものをシリコーン変性した例であり、比較  
例3と同様に塗面状態の欠陥が生じている。又、  
耐グーストヘリヤ性、ワキ膜厚等も劣っている。  
樹脂の高価性に起因する原料分散性不足、相溶性  
不足、表面硬化(皮膜)等の為と思われる。比  
較例5と6はアルキド樹脂を用いた例であり、乾  
燥前及び乾燥後の耐ワックス耐性、層間付着性、  
促進耐腐蝕試験での充保保持性などが劣っている。  
比較例7はアクリル樹脂を用いた例であり塗面の

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同押圧が不足し、耐ワットスがけ性、層間付着性、  
ワヤ、タレ限界部厚等が劣っている。以上のこと  
から本発明のシリコーン変性ポリエステル系上塗  
り塗料組成物は非常に優れた性能を有することが  
明らかである。

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ほか 3 名

Dnp.

SHUSAKU YAMAMOTO

Re: Validity Searches for U.S. Patent No. 5,066,720 ✓

Translation of P-5 (Japanese Laid-Open Publication No. 56-157461)

Laid-Open Publication Date: December 4, 1981

Application Number: 55-59897

Filing Date: May 8, 1980

Inventors: Yorio DOI, et al.

Patentee: KANSAI PAINT CO. LTD.

SPECIFICATION

1. Title of the Invention: SILICONE-MODIFIED POLYESTER TOP-COAT PAINT COMPOSITION

2. Claims

1. A silicone-modified polyester topcoat composition, comprising, as its essential components, (A) a silicone-modified polyester, (B) a binder component consisting of amino-aldehyde resin and/or block isocyanate, and (C) a pigment, wherein: at least 25 mol% of an acid component of the polyester of the component (A) is a saturated alicyclic polybasic acid; the component (A) is obtained by modifying 75-97 parts by weight of an oil-free saturated polyester resin whose hydroxyl value is 60-200 with 3-25 parts by weight of a reactive organopolysiloxane resin whose molecular weight is about 500 to about 2,000; the content ratio between the component (A) and the component (B) is 60-90 parts by weight of (A) for 10-40 parts by weight of (B); and the pigment content is 3-100 PHR.

2. A composition according to claim 1, wherein the acid component of the polyester comprises not only the saturated alicyclic polybasic acid but also one selected from the group consisting of an aromatic polybasic acid and a linear-chain saturated dibasic acid represented by the general formula  $\text{HOOC}(\text{CH}_2)_n\text{COOH}$  (where n is an integer of 1-12).

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3. A composition according to claim 2, wherein the total amount of the saturated alicyclic polybasic acid and the aromatic polybasic acid is 70 mol% or more, and the content of the aromatic polybasic acid is 55 mol% or less.

3. Detailed Description of the Invention

The present invention relates to a topcoat paint composition for use in spray coating, comprising silicone-modified polyester/amino-aldehyde resin and/or block isocyanate.

Amino-alkyd resin paints, amino-acrylic resin paints, acrylic lacquer paints, and the like, are conventionally known in the art as topcoat paints for automobile bodies. The amino-alkyd resin paints are characterized in that they are easy to apply and have good finish appearance (the gloss of the applied film, the thick touch, etc.), and a good weather resistance for high pigment concentration ranges (the gloss retention). However, a so-called "dark color" coating film, i.e., a coating film in which the pigment concentration is low and the pigment contains a large amount of pigment other than white (hereinafter, referred to as a "coloring pigment") has a poor waxing resistance as will be discussed below. That is, when waxing on such a coating film, the film is likely to get scratched or lose its gloss, and the waste cloth used for waxing is likely to get colored considerably. While the waxing resistance is required in a coating film immediately after application thereof and after outdoor exposure thereof, it is difficult to obtain a satisfactory waxing resistance with an amino-alkyd resin topcoat paint. The amino-acrylic resin topcoat paint is quite desirable in its weather resistance for low pigment concentration ranges (40-30 PHR or less), but the waxing resistance before exposure is not always desirable. Especially, it is difficult to satisfy the requirements such



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as the properties required for a topcoat on an automobile body, i.e., non-sand interlayer adhesion (i.e., the adhesion between two coating films when the first coat is applied and baked, after which the same paint is again applied and baked onto the first coat for touchup), the Erichsen test, the shock resistance, and the finish appearance (the gloss of the applied film, the thick touch, etc.). The acrylic lacquer paints have a significantly low as-applied solid component concentration, and it is necessary to provide many application steps.

Oil-free polyester/amino-aldehyde resin paints have advantages over the above-described paints such as a good weather resistance, good mechanical properties in the applied film (the Erichsen test, the shock resistance), a good interlayer adhesion, and a high as-applied solid component concentration. However, it has been believed that it is difficult to use such paints particularly as a topcoat on an automobile body because: it is difficult to apply (e.g., repelling is likely to occur); the surface of the applied film is "blurred", so to speak, and the gloss is poor; and the compatibility with an amino resin is poor.

It has been proposed (Japanese Patent Application No. 54-94269) to use an oil-free polyester resin having a special composition to obtain an oil-free polyester/amino-aldehyde resin topcoat paint with improvements in terms of the gloss, repelling resistance, compatibility with an amino resin, and the ease of application (i.e., the application property).

An object of the present invention is to provide a topcoat paint composition which has the advantages of oil-free polyesters and in which the application property, the gloss of the applied film, the repelling resistance, etc., (particularly, the application property) are further im-

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proved from those of the above-described paint in the prior art.

The object of the present invention is realized by a silicone-modified polyester topcoat composition, comprising, as its essential components, (A) a silicone-modified polyester, (B) a binder component consisting of amino-aldehyde resin and/or block isocyanate, and (C) a pigment, wherein: at least 25 mol% of an acid component of the polyester of the component (A) is a saturated alicyclic polybasic acid; the component (A) is obtained by modifying 75-97 parts by weight of an oil-free saturated polyester resin whose hydroxyl value is 60-200 with 3-25 parts by weight of a reactive organopolysiloxane resin whose molecular weight is about 500 to about 2,000; the content ratio between the component (A) and the component (B) is 60-90 parts by weight of (A) for 10-40 parts by weight of (B); and the pigment content is 3-100 PHR.

The excellent application property of the paint composition of the present invention has been achieved mainly due to a successful and balanced suppression of the undesirable phenomena of "running" and "bubbling" which may occur in paint application.

Generally, the term "running" refers to a phenomenon where a paint which is applied onto a vertically standing painting substrate by, for example, spray application, runs down along the substrate due to gravity. A paint applied onto a painting substrate is required to stay where it is applied without having the running phenomenon. Otherwise, the film thickness will be substantially uneven, or a flow pattern occurs on the application surface, whereby a desirable application surface cannot be obtained.

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The occurrence of such a running phenomenon rapidly increases as the thickness of the applied film increases over a certain value. The thickness past which the occurrence of running rapidly increases is called the "running critical thickness". A paint having a higher running critical thickness is considered to have a good application property, in other words, it is a paint which is easy to apply.

The term "bubbling" refers to a phenomenon where a baking-finish-type paint, after it is taken out of a baking furnace, has an indicative trace of a bubble or a bubble itself on the application surface. It is believed that bubbling occurs due to rapid evaporation of a solvent in the paint during baking or passage of an air bubble which has been trapped during application. The occurrence of this phenomenon also rapidly increases when the thickness of the applied film increases over a certain value. Such a critical thickness is called the "bubbling critical thickness". The higher this value is, the better the application property is.

Thus, a paint having a high running critical thickness and a high bubbling critical thickness is an easy-to-apply paint. However, the two values are typically in a trade-off relationship, and it is in many cases difficult to have both values high. In other words, if one of the values is increased, the other will decrease, and it is difficult to obtain a paint which has both values high. For example, the bubbling critical thickness can be increased by using a large amount of a solvent which has a high boiling point and is less likely to evaporate. However, this slows down the viscosity increase rate of the applied paint, and as a result the applied paint is more likely to run, thereby lowering the running critical thickness.

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Typically, with an oil-free polyester, as compared with an alkyd resin or an acrylic resin, it is difficult to maintain a high level and good balance of running and bubbling. However, when a particular oil-free polyester is modified with a small amount of silicon resin according to the present invention, surprisingly, it is possible to obtain a high level and good balance of running and bubbling.

Silicone-modified polyester or silicone-modified alkyd resins have conventionally been used as a pre-coat metal paint (e.g., Japanese Laid-Open Publication No. 47-21493). However, such a conventional silicone-modified resin comprises a large amount, 30 wt% or more, of a silicone resin so as to improve the heat resistance and the weather resistance of the resin paint.

On the contrary, the present invention significantly improves the application property of a spray topcoat paint by modifying a particular polyester with a small amount of silicone.

An oil-free polyester to be a substrate resin of a silicone-modified polyester for use with the present invention is characterized in that it comprises a saturated alicyclic polybasic acid (a) in an amount of at least 25 mol%, and preferably at least 40 mol%, of the total acid component. The other acid component, i.e., the polybasic acid material, of the polyester may be an aromatic polybasic acid (b) and/or a linear-chain saturated dibasic acid (c) represented by the general formula  $\text{HOOC}(\text{CH}_2)_n\text{COOH}$  (where n is an integer of 1-12). Moreover, in order to prepare a preferable substrate polyester, it is desirable that the total amount of the polybasic acid components (a) and (b) is 70 mol% or more and that the content of the component (b) is 55 mol% or more.

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When the total amount of the polybasic acid components (a) and (b) is less than 70 mol%, the weather resistance and/or the acid resistance decrease. When the content of the component (b) exceeds 55 mol%, the compatibility between the substrate polyester and the silicone resin as a modifier may decrease, thereby making it more difficult for the reaction to modify an oil-free polyester with a silicone resin to progress. Moreover, the compatibility between the produced silicone-modified polyester and the amino-aldehyde resin as a crosslinking agent decreases, thereby causing deficiencies on the application surface (insufficient gloss) and/or decreasing the solvent resistance.

The hydroxyl value of the oil-free polyester is required to be in the range of 60-200, and preferably in the range of 80-150. When the value is less than or equal to 60, the applied film will not be cured sufficiently. When the value is equal to or greater than 200, the dispersibility of the pigment and the compatibility thereof with a crosslinking agent decrease.

Examples of the saturated alicyclic polybasic acid (a) forming the oil-free polyester used in the present invention include hexahydroisophthalic acid, hexahydroterephthalic acid, hexahydrophthalic acid and anhydride thereof, a methylhexahydrophthalic acid and anhydride thereof, hexahydrotrimellitic acid and anhydride thereof, hexahydro-2-methyltrimellitic acid and anhydride thereof, and the like. Examples of the aromatic polybasic acid (b) include phthalic acid and anhydride thereof, isophthalic acid, terephthalic acid, dimethylisophthalic acid, dimethylterephthalic acid, trimellitic acid and anhydride thereof, pyromellitic acid and anhydride thereof, and the like. The examples of the linear-chain saturated dibasic acid (c) represented by the general formula  $\text{HOOC}(\text{CH}_2)_n\text{COOH}$  include succinic acid (and

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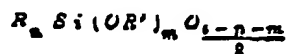
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anhydride thereof), adipic acid, pimelic acid, azelaic acid, sebacic acid, brasylic acid, and the like.

On the other hand, the alcohol component of the oil-free polyester is not so limited and may be those that are commonly used in the prior art for producing a polyester. For example, ethylene glycol, diethylene glycol, propylene glycol, neopentyl glycol, 1,2-butylene glycol, 1,3-butylene glycol, 2,3-butylene glycol, 1,4-butylene glycol, 1,6-hexanediol, 1,5-pentanediol, 1,6-hexanediol, 2,5-hexanediol, trimethylolethane, trimethylolpropane, glycerin, pentaerythritol, dipentaerythritol, diglycerin, sorbitol ester diol 204 (manufactured by Union Carbide Corporation (U.S.)), tricyclodecanedimethanol, 1,4-cyclohexanedimethanol, and the like, are contemplated.

The oil-free polyester to be a substrate resin of a silicone-modified polyester can be produced by a common condensation polymerization of the saturated alicyclic polybasic acid (a) and the aromatic polybasic acid (b), and optionally the linear-chain saturated dibasic acid (c), with at least one of the above-listed alcohols. In this process, the molecular weight may be adjusted by using, for example, benzoic acid, p-t-butyl benzoic acid, methyl benzoate, or the like, as a terminal blocking agent. The reaction ratio between the polybasic component and the alcohol component is adjusted so that the hydroxyl value of the obtained oil-free polyester is 60-200, and preferably 80-150.

The silicone resin used in the present invention to modify the substrate polyester is an organopolysiloxane resin having a number average molecular weight of about 500 to about 2000 which is represented by the following unit formula:

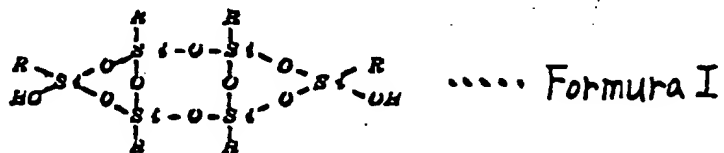



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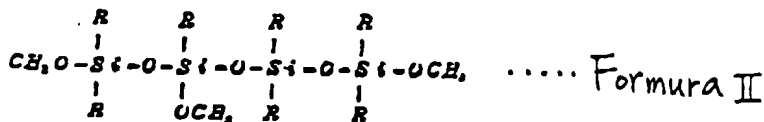
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where R denotes a monovalent organic group which binds to silicon via carbon-silicon bond, R' denotes hydrogen, an alkyl group or an aryl group of C<sub>1</sub>-C<sub>20</sub>. In the above formula, each of n and m is a number less than or equal to 4, and n+m has to be less than or equal to 4.

The silicone resin used in the present invention preferably includes, in each molecule, two or more of the reactive group such as a hydroxyl group or an alkoxy group represented by (OR') in the above formula. Such a silicone resin includes Z-6018 (manufactured by Dow Corning, molecular weight: 1600, a definition of R represented by Formula I)



[R denotes CH<sub>3</sub> or , and Z-6188 (manufactured by Dow Corning, molecular weight: 650, a definition of R represented by Formula II)



[R denotes CH<sub>3</sub> or , as well as Sylkyd 50, DC-3037 (manufactured by Dow Corning), KR-216, KR-218, KSP-1 (manufactured by Shinetsu Silicone), TSR-160, TSR-165 (manufactured by Toshiba), SH5050, SH6018, SH6188 (manufactured by Toray Silicone), and the like.

When producing a silicone-modified polyester by modifying a substrate polyester with a silicone resin according to the present invention, the amount of the silicone

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resin to be used is, in terms of the ratio between the substrate polyester and the silicone resin, 3-25 parts by weight for 97-75 parts by weight of the substrate polyester, and preferably 7-18 parts by weight for 93-82 parts by weight of the substrate polyester. When the content of the silicone resin is 3 parts by weight or less, the pigment dispersibility, which is an advantage of the silicone-modified polyester, decreases, thereby causing deficiencies such as blurring of the application surface, and reducing the application workability, e.g., repelling is likely to occur. On the other hand, when the content of the silicone resin is 25 parts by weight or more, the resin cost becomes high, and the alkali resistance and the curing property decrease, thereby losing its suitability as a topcoat paint.

The silicone-modified polyester used in the present invention can be produced by using a method which is per se known in the art to copolymerize the substrate polyester and the silicone resin at the above-described ratio. The reaction is suitably performed in the presence or absence of a solvent by heating the materials to a temperature of 200°C or less, and preferably 150°C or less. As the solvent used herein, a solvent which is commonly used in a paint such as aromatic solvents, esters, ketones, petroleums, or the like, may be selected in view of the relationship between the boiling point thereof and the co-condensation reaction temperature. An alcohol solvent is not preferred because it reduces the rate of the co-condensation reaction. It is preferred to use a condensation catalyst in order to promote the co-condensation reaction. The condensation catalyst used herein may be iron octenoate, zinc octenoate, potassium hydroxide, p-toluenesulfonic acid, tin(II) octenoate, tetraalkyl titanate, hydrochloric acid, phosphoric acid, a higher fatty acid, maleic anhydride, or the like.



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The present invention significantly improves the application property by using as a topcoat paint resin a silicone-modified polyester which is obtained by modifying a particular polyester with a small amount of silicone resin (3-25 wt%) as described above. The application property as used herein refers to an increased bubbling and/or running critical thickness as the applied film is cured by heating, and to a property of preventing repelling and/or indentation when a heterologous dust (e.g., amino-alkyd resin paint, or an amino-acrylic resin paint) is put on an uncured applied film before the heat-drying process. The silicone modification also has other advantages, associated with the above advantages, e.g., an increase in the dispersibility of a pigment, an increase in the compatibility and solubility with a solvent and thus an increase in the solid component concentration in the spray application. Moreover, with the topcoat paint of the present invention, the gloss and the vividness of the applied film are much better than those of a conventional oil-free polyester topcoat paint. Such advantages are achieved only by using a resin obtained by modifying a polyester having a particular composition disclosed herein with an amount of silicone in the range of 3-25 wt%. The topcoat paint of the present invention is especially desirable as a topcoat paint for automobiles. When a polyester having a composition other than those specified herein is modified with a silicone, there would only be little improvement in the application property, and a sufficient practicability as a topcoat paint for automobiles cannot be obtained.

The amino-aldehyde resin used in the present invention as the crosslinking component (B) may be any of most amino-aldehyde resins commonly used as a paint, and the amino component thereof may be melamine, urea, benzoguanamine, acetoguanamine, steroguanamine, spiroguanamine, or the like. In view of the weather resistance, the most preferred resin

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is a melamine formaldehyde resin. A common curing catalyst may be added to such an amino-aldehyde resin in order to lower the curing temperature.

The block-type polyisocyanate may be produced by turning yellowing-free polyisocyanate into a block-type polyisocyanate with a common blocking agent such as, for example, an aliphatic or aromatic monoalcohol, phenol, oxime, or caprolactam. For example, Takenate B-815N (manufactured by Takeda Chemical Industries, Co., Ltd.), Takenate B-840N (manufactured by Takeda Chemical Industries, Co., Ltd.), Ad-duet B1065 (Veba Chemie (Germany)), or ADDITOL VXL-80 (manufactured by Hoechst Japan Ltd.) may be used. When such a block-type polyisocyanate is used, a catalyst for facilitating the dissociation of a blocking agent may be optionally added.

The above-described amino-aldehyde resin and the block-type polyisocyanate may be used alone or in combination.

The binder component composition in the paint composition of the present invention needs to be in the range of 90/10-60/40 in terms of the weight ratio between the silicone-modified polyester and the amino-aldehyde resin and/or block-type polyisocyanate. When the content of the amino-aldehyde resin and/or block-type polyisocyanate as a crosslinking agent is below this range, the curing will be insufficient, thereby lowering the weather resistance, the hardness of the applied film, the solvent resistance, and the like. When the content of the crosslinking agent is above this range, the applied film will be brittle.

While the pigment concentration of the paint composition of the present invention may be 100 PHR or less, the concentration is typically required to be 3 PHR or more

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in order to completely cover an underlying layer with a thickness (about 20-50  $\mu$ ) which is commonly-employed with a topcoat paint for automobile bodies, or the like. When the concentration is 100 PHR or more, the weather resistance will be on the same level as that of an amino-alkyd resin topcoat paint, thereby detracting from the advantages of the present invention.

The paint composition of the present invention has a good waxing resistance before and after exposure and has a particularly desirable waxing resistance in the case where paint contains a large amount of coloring pigment. The effects of the present invention are particularly pronounced when the weight ratio of the coloring pigment/titanium white pigment in the pigment is in the range of 100/0-30/70, and preferably 100/0-60/40.

An automobile body can be painted with a paint composition of the present invention as follows. First, a paint is produced by a common method by mixing a binder component consisting of the silicone-modified polyester component (A) and the crosslinking component (B) with a commonly used coloring pigment, and optionally an additive. The produced paint is adjusted by a dilution solvent so that the paint viscosity is 20-30 sec as measured with a Ford cup No. 4 (20°C). Then, the paint is applied on a painting substrate having a first coat, and optionally a second coat, applied thereon so that the applied film after being dried has a thickness of about 20-60  $\mu$ . The application method may be a common air spray method, an airless spray method, electrostatic application method, or the like. Then, the applied paint is left standing at room temperature for a few minutes, after which it is heated to 80-160°C for 20-40 min, thereby obtaining a topcoat.

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The silicone-modified polyester topcoat paint composition of the present invention has a level of performance comparable to that of an amino-alkyd resin paint, which is most commonly used as a topcoat for automobiles, in terms of the application property, the pigment dispersibility, the appearance of the applied film, the mechanical properties, the chemical resistance and the solvent resistance of the applied film, among other properties required for a topcoat on an automobile. For the weak points of an amino-alkyd resin paint, i.e., the weather resistance for low pigment concentration ranges (the gloss retention) and the waxing resistance before and after exposure, the paint composition of the present invention is much better than an amino-alkyd resin paint. Moreover, the paint composition of the present invention is also better than an amino-alkyd resin paint in terms of the interlayer adhesion. Furthermore, as compared to an amino-alkyd resin paint, the paint composition of the present invention is much superior in terms of the weather resistance (the gloss retention), the interlayer adhesion, the mechanical properties of the applied film. The paint composition of the present invention has a particularly desirable waxing resistance before and after exposure when used in a paint having a color which has a high chroma, e.g., dark green, dark maroon, or dark blue, which contains a large amount of a coloring pigment.

As described above, the paint composition of the present invention is significantly desirable in terms of the application property, the weather resistance and the pigment dispersibility. Therefore, beside automobile bodies, the paint composition of the present invention can be widely used in other household or industrial spray paints which are required to have a gloss in the applied film, the thick touch and the weather resistance.

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The present invention will now be described by way of examples. In the examples, "parts" and "%" denote "parts by weight" and "wt%" unless otherwise noted.

Production Example 1

Production of oil-free polyester resin solution A

53.9 parts (0.35 mol) of hexahydrophthalic anhydride, 58.1 parts (0.35 mol) of isophthalic acid, 29.2 parts (0.2 mol) of adipic acid, 40.8 parts (0.3 mol) of trimethylolpropane, and 73.5 parts (0.7 mol) of neopentyl glycol are charged into a reaction chamber equipped with a heating device, a stirrer, a reflux device, a water separator, a rectifier and a thermometer, and heated. When the materials are melted so that they can be stirred, stirring is started, and the reaction chamber temperature is raised to 230°C. Herein, from 160°C to 230°C, the temperature is raised at a uniform rate for 3 hours, and generated condensation water is distilled out of the system.

When the temperature reaches 230°C, the temperature is kept constant and stirring is continued for 2 hours. Thereafter, xylol is added to the reaction chamber, and the reaction is switched to a condensation in the presence of a solvent, letting the reaction continue. When the acid value reaches 7, the reaction is terminated and the reaction chamber is cooled down. After the cooling, 100.6 parts of Suwazol #1500 (manufactured by Maruzen Sekiyu Kagaku) and 43.1 parts of cellosolve acetate were added to produce an oil-free polyester solution A. The oil-free polyester solution A had a solid component concentration of 60.0%, a varnish viscosity of V (Gardner viscosity, 25°C), an acid value of 7.0, and a hydroxyl value of 122.

Production Examples 2-10

Production of oil-free polyester resin solutions B-J

1 20 2000 20.11 20.11.11 1.00/11

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Using the material components as shown in Table 1, oil-free polyester resin solutions B-J were produced in a manner similar to that of Production Example 1. The varnish characteristic values of the solutions are shown in Table 1. The resin solutions A-F are used in the examples of the present invention, and solutions G-J are used in comparative examples.



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**Production Example 11**

**Production of silicone polyester resin solution K**

150.0 parts (solid component: 90) of the oil-free polyester resin solution A, 11.2 parts (solid component: 10) of silicone intermediate SH6188 (a silicone resin represented by Formula I above, manufactured by Toray Silicone), and TPT (A-1) (tetraisopropyl titanate, manufactured by Nippon Soda Co., Ltd.) as a condensation catalyst are charged into a reaction chamber equipped with a heating device, a stirrer, a water separator, and a thermometer, and heated while being stirred. When the reaction temperature reaches 140°C, the temperature is kept constant. Generated methanol is distilled out of the system. The reaction product is applied in a thin layer on a glass plate, and forcibly dried (130°C x 20 min). Both before the drying and after the drying, the reaction is continued until the resin is completely dissolved and becomes clear. At a point of time the resin is clear and the Gardner bubble viscosity is 4 sample or more higher than the initial viscosity (after cold mixing), the reaction is terminated and the reaction chamber is cooled down. After the cooling, 5 PHR of n-butanol and a mixed solvent of Suwazol #1500/cellosolve acetate=70/30 were added, and the solid component concentration is adjusted to 60%. The silicone polyester resin solution K had a solid component concentration of 59.8% and a varnish viscosity of X (Gardner viscosity, 25°C).

**Production Examples 12-22**

Silicone polyester resin solutions L-V were produced in a manner similar to that of Production Example 11 based on the resin contents shown in Table 2. The varnish characteristic values of the solutions are shown in Table 2. The resin solutions K-Q, U and V are used in the examples of the present invention, and the resin solutions R-T are used in the comparative examples. When producing silicone polyester solutions M and P, 11.4 parts of DC-3037 (a silicone



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resin represented by Formula II above, manufactured by Dow Corning) is charged instead of 11.2 parts of silicone intermediate SH6188. Thereafter, the silicone polyester solutions M and P are produced in a manner similar to that of Production Example 11.

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Table 2

content of resin solution	L	M	N	O	P	Q	R	S	T	U	V
name of polyester solution	B	C	D	E	F	G	H	I	J	A	A
content of silicone intermediate	1505	1503	1510	1485	1488	1505	1480	1500	1513	1523	1523
name of silicone intermediate	SH 6188	DC- 3037	SH 6188	SH 6188	DC- 3037	SH 6188	SH 6188	SH 6188	SH 6188	SH 6188	SH 6188
content of silicone intermediate	112	112	112	112	112	112	112	112	112	112	225
Solid component concentration(%)	602	602	601	603	600	599	602	601	597	520	603
varnish viscosity	WX	V	Z	Z, Z,	T	ZZ,	U	Z,	P	X	YZ
amount of silicone modified (%)	10	10	10	10	10	10	10	10	10	5	20

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Production Example 23

Production of alkyd resin solution W

An alkyd resin solution W was produced in a manner similar to that of Production Example 1. The resin composition was as follows: phthalic anhydride 133.2 parts (0.9 mol), trimethylolpropane 136 parts (1.0 mol), coconut oil fatty acid 105 parts (0.5 mol). The resin solution had a solid component concentration of 60.3%, a varnish viscosity of P, a resin acid value of 7.0, and a resin hydroxyl value of 105. The varnish solvent is xylol/isobutanol=60/40.

Production Example 24

Production of acrylic resin solution X

An acrylic resin solution X having the following composition was prepared using azobisisobutyronitrile as a condensation catalyst. The acrylic resin solution X had a solid component concentration of 50.0%, a varnish viscosity of T (Gardner viscosity, 25°C), and a resin acid value of 15.4. The varnish solvent is xylol/n-butanol=80/20.

Composition of acrylic resin solution X

styrene	30 parts
n-butyl methacrylate	30 parts
n-butyl acrylate	20 parts
2-hydroxyethyl methacrylate	18 parts
acrylic acid	2 parts

[Preparation of painting substrate]

A polybutadiene electrodeposition paint is applied by using an electrodeposition coating method onto a door part of an automobile body, which has been subjected to a zinc phosphate treatment so that the thickness of the film after being dried is 20  $\mu$ , and baked at 170°C for 20 minutes. Then, the application surface is polished with a #400 sandpaper, and then the surface is wiped off using a gauze dampened with petroleum benzin, thereby degreasing the sur-

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face. Thereafter, an amino-alkyd resin intermediate paint for automobiles is applied so that the thickness of the film after being dried is 25  $\mu$ , and baked at 140°C for 30 min. Then, the application surface is wet-sanded with a #400 sandpaper, drained/dried, and the application surface is wiped off using petroleum benzin, thereby obtaining the painted substrates of the examples of the present invention and those of the comparative examples.

Example 1

Using the silicone-modified polyester resin solution K obtained in Production Example 11 above, a maroon color topcoat paint having the following composition was produced by ball mill dispersion.

60% silicone-modified polyester resin solution K		117 parts
60% Yuban 28SE	(see Note 1)	50 parts
Perindo Maroon R-6422	(see Note 2)	10 parts
Toda Color KN-0	(see Note 3)	1 parts
NeO Spectra Beads AG	(see Note 4)	0.3 part

(Note 1) a melamine resin manufactured by Mitsui Toatsu Kagaku

(Note 2) Maroon organic pigment manufactured by Bayer (Germany)

(Note 3) Iron Oxide Red manufactured by Toda Kogyo

(Note 4) Carbon black manufactured by Columbia Carbon (U.S.)

0.05 PHR of Modaflow (manufactured by Monsanto) and 0.01 PHR of silicone oil KP-323 (manufactured by Shinetsu Kagakusha) were added to the paint as an application surface conditioner.

The obtained paints were diluted to a viscosity of 25 sec (Ford cup No. 4, 20°C) by using a mixed solvent of Sukuzol #1500/xylol/butyl acetate/n-butanol-30/20/30/20.

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The diluted paint was air-sprayed on a painting substrate prepared in advance so that the thickness of the film after being dried is 30  $\mu$ , and left standing at room temperature for 10 min. Then, the sprayed paint was baked for 30 min at a temperature of 140°C by using an electric hot air dryer. The test results for the resultant painted plate are shown in Table 4.

Examples 2-12, Comparative Example 1-7

Using each of the silicone-modified polyesters obtained in the production examples above, a paint was produced in a manner similar to that of Example 1 based on the paint composition shown in Table 3. The produced paint was applied on a painting substrate.

The test results are shown in Table 4.

Table 3

No.	Composition
Example 2	60% silicone-modified polyester 117 parts
	resin solution K
	60% Yuban 28SE 50
	Titanium White JR-602 40
	(Manufactured by Teikoku Kako)
Example 3	60% silicone-modified polyester 117 parts
	resin solution L
	60% Yuban 28SE 50
	phthalocyanine green GBN 15
	(Manufactured by ICI (U.K.), Green organic pigment)
	Toda Color KN-0 3
Example 4	NeO Spectra Beads AG 0.2
	60% silicone-modified polyester 125 parts
	resin solution M
	60% Yuban 28SE 42
	Cyanin Blue-5023A 8
	(pigment manufactured by Dainippon Ink Kagaku Kogyo)

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	Titanium White JR-602	5
Example 5	60% silicone-modified polyester resin solution M	117 parts
	60% Yuban 28SE	42
	Takenate B-815N	8.3
	(Manufactured by Takeda Chemical Industries, Co., Ltd., block type polyisocyanate, solid component: 60%)	
	Formate TK-1	0.1
	(Manufactured by Takeda Chemical Industries, Co., Ltd., dissociation catalyst for block type polyisocyanate)	
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Example 6	60% silicone-modified polyester resin solution N	117 parts
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Example 7	60% silicone-modified polyester resin solution O	117 parts
	60% Yuban 28SE	42
	ADDITOL VXL-80	5
	(manufactured by Hoechst Japan Ltd., block type polyisocyanate)	
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Example 8	60% silicone-modified polyester resin solution O	117 parts
	60% Yuban 28SE	42
	ADDITOL VXL-80	5
	phthalocyanine green GBN	15
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Example 9	60% silicone-modified polyester	108 parts

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	resin solution P	
	60% Yuban 28SE	50
	Takenate B-815N	8.3
	Formate TK-1	0.1
	Cyanin Blue 5023A	8
	Titanium White JR-602	5
Example 10	60% silicone-modified polyester	117 parts
	resin solution U	
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Example 11	60% silicone-modified polyester	117 parts
	resin solution V	
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Example 12	60% silicone-modified polyester	117 parts
	resin solution Q	
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Comparative Example 1	60% polyester resin solution A	117 parts
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Comparative Example 2	60% silicone-modified polyester	117 parts
	resin solution R	
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Comparative	60% silicone-modified polyester	117 parts

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Example 3	resin solution S	
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
Comparative Example 4	60% silicone-modified polyester	117 parts
	resin solution T	
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
Comparative Example 5	NeO Spectra Beads AG	0.3
	60% alkyd resin solution W	117 parts
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
Comparative Example 6	NeO Spectra Beads AG	0.3
	60% alkyd resin solution W	117 parts
	60% Yuban 28SE	42
	Takenate B-815N	8.3
	Formate TK-1	0.1
Comparative Example 7	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3
	50% acrylic resin solution L	140 parts
	60% Yuban 28SE	50
	Perindo Maroon R-6422	10
	Toda Color KN-0	1
	NeO Spectra Beads AG	0.3



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Table 4

Performance of applied film	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
finish appearance (gloss, the thick touch, etc.). (see Note 1)	◎	◎	○	◎	◎	◎	◎	◎
60° mirror reflectance	93	97	92	98	98	98	97	97
pencil hardness	F	H	H	F	F	H	H	H
Shock resistance (cm) (Du Pond measurement, $\varphi = 1/2"$ , 500g)	40	30	35	40	40	30	35	35
Erichsen value (mm)	4.2	2.7	4.2	4.7	5.0	3.2	4.0	2.9
gasoline wiping resistance (see Note 2)	good	good	good	good	good	good	good	good
acid resistance (see Note 3)	normal	normal	normal	normal	normal	normal	normal	normal
Waxing resistance (before exposure) (see Note 4)	◎	◎	○	○	○	○	◎	○
Waxing resistance (sunshine weatherometer, after 400 hours) (see Note 4)	○	○	○	○ <sup>-</sup>	○ <sup>-</sup>	○	○	○
weather resistance (sunshine weatherometer, gloss retention after 800 hours) %	90	93	91	91	92	91	93	89
interlayer adhesion (see Note 5)	○	○	○	○	○	○	○	○
dust repelling resistance (see Note 6)	○	○	○	○	○	○	○	○
Bubbling critical thickness, $\mu$ (see Note 7)	>50	>50	>50	>50	>50	>50	>50	>50
Running critical thickness, $\mu$ (see Note 8)	>50	>50	>50	50	50	>50	>50	>50

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Table 4 (continued)

Example 9	Example 10	Example 11	Example 12	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7
96	92	95	90	91	95	84	70	94	93	94
F	F	F	HB	F	B	H	SH	F	F	F
20	40	40	40	40	40	30	35	25	30	20
27	43	40	45	45	50	34	08	40	42	20
good	good	good	good	good	glass burred	good	good	good	good	substantial scratch
normal	normal	normal	normal	normal	discoloring, blistering	normal	normal	normal	normal	normal
90	95	89	85	80	70	90	50	82	72	88
0	0	0	0	0	0	0	0	X	X	X
0	0	0	0	0	0	0	0	X	X	0
>50	>50	>50	>50	35	>50	>50	44	50	50	38
50	50	>50	>50	40	60	>50	>50	56	50	33

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(Note 1) The finish appearance was evaluated in terms of the thick touch based on the following criteria.

◎: Very good

○: Good

⊕: Fair

△: Poor

X: Very poor

(Note 2) Gasoline wiping resistance: A gauze was dampened with Nisseki Silver Gasoline, and the application surface was strongly rubbed with the gauze over a length of 10 cm for 8 reciprocations, after which the application surface was observed. Those having substantially no scratch or gloss blurring on the application surface were considered as "good".

(Note 3) Acid resistance: 0.5 cc of 10% sulfuric acid was dropped onto the application surface, and left standing at 20°C, 75 %RH for 48 hours. Then, the application surface was washed with water, and observed.

(Note 4) Waxing resistance: A small amount of a car wax "Soft 99 Hanneri" (manufactured by Nitto Kagaku) was applied on a piece of white flannel cloth, and the application surface was strongly rubbed with the cloth by using the index finger over a length of 10 cm for 10 reciprocations. Thereafter, the wax remaining on the application surface was removed with a new piece of flannel cloth, and then the application surface was observed. The gloss blurring and scratch on the application surface and the degree of coloring of the white flannel cloth were comprehensively evaluated based on the following criteria.

◎: No gloss blurring or scratch on application surface and no coloring of flannel cloth

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○: Substantially no gloss burring or scratch on application surface and substantially no coloring of flannel cloth

○<sup>-</sup>: Slightly poorer than ○ but better than ⊗

⊗: Slight gloss burring and/or scratch on application surface and slight coloring of flannel cloth observed (threshold for practical use)

△: Considerable gloss burring and/or scratch on application surface and considerable coloring of flannel cloth

×: Significant gloss burring and/or scratch on application surface and significant coloring of flannel cloth

(Note 5) The painted plates produced in the examples and the comparative examples are further over-baked at 160°C for 90 min, and then the respective topcoat paints are sprayed and baked at 120°C for 30 min (Each topcoat paint is over-coated with the same topcoat paint). Thereafter, the application surface is scratched with a cross cut using a razor, and a peeling test is performed with a cellophane tape. The over-coated films which do not peel from each other are marked with ○, and those which peel from each other are marked with ×.

(Note 6) Dust repelling resistance: Paints used in the examples and the comparative examples are air-sprayed onto a painting substrate, and left standing at room temperature for 3 min. Thereafter, an amino-alkyd resin topcoat paint for automobiles in the form of mist is sprayed onto the painting substrate. After standing for 10 min, the paint is baked at 140°C for 30 min, and the state of the mist paint on the application surface was evaluated.

○: Paint is cured while remaining the form of fine mist as applied. The application surface appears normal.

⊗: Mist pattern is spread.

△: Mist portion is indented.

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X: Mist paint is spread and repelled all over the application surface.

(Note 7) Bubbling critical thickness: Each of the paints used in the examples and the comparative examples is applied at a discharge rate of 200 cc/min onto a horizontal painting substrate with a thickness gradient such that the thickness of the film after being dried gradually increases from the left-hand side of the painted plate to the right-hand side thereof, and left standing at room temperature for 10 min. Thereafter, the applied paint is baked at a temperature of 140°C for 30 min by using an electric hot air dryer. The thickness of the location of the application surface at which a significant level of bubbling starts to appear is measured as the bubbling critical thickness.

(Note 8) Running critical thickness: Each of the paints used in the examples and the comparative examples is applied in a manner as described in (Note 7) onto an inclined painting substrate with a thickness gradient. The painting substrate is provided with holes having a diameter of 6-8 mm in advance. After the application, the applied paint is left standing for 10 min with the painting substrate being inclined, and baked at a temperature 140°C for 30 min by using an electric hot air dryer. The inclination angle of the painting substrate needs to be kept at 60° or more with respect to the horizontal plane until the end of the evaluation. After drying, the thickness of the location of the application surface around the hole portion at which running starts to appear is measured as the running critical thickness.

Examples 1-12 are silicone polyester topcoat paint compositions of the present invention, and each of them exhibits a good property in each test. Comparative Example 1 is a case where an unmodified oil-free polyester is used,

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and is slightly poorer in terms of the application property, e.g., the dust repelling resistance, the bubbling critical thickness and the running critical thickness, as compared to a silicone-modified polyester. Comparative Example 2 uses an oil-free polyester resin whose hydroxyl value is less than 60. Therefore, the curing is insufficient, whereby the paint is inferior in terms of the hardness, the gasoline wiping resistance, the shock resistance, the waxing resistance, etc. Comparative Example 3 is a case where the content of the aromatic polybasic acid (isophthalic acid) in the polybasic acid component of an oil-free polyester resin is over 55 mol%. Comparative Example 3 has deficiencies in the appearance of the application surface, e.g., insufficient gloss, and insufficient luster, due to the poor compatibility with the amino-aldehyde resin. Comparative Example 4 is an example where an oil-free polyester resin whose hydroxyl value is 200 or more is modified with a silicone, and has deficiencies as those in Comparative Example 3. Comparative Example 4 is also inferior in terms of the dust repelling resistance, the bubbling critical thickness, etc. This appears to be because of the insufficient pigment dispersibility, the insufficient compatibility, the surface hardening (skinning), etc., which are due to the high polarity of the resin. Each of Comparative Examples 5 and 6 is an example where an alkyd resin is used, and inferior in terms of the waxing resistance before and after exposure, the interlayer adhesion, and the gloss retention in the promoted weather resistance test. Comparative Example 7 is an example where an acrylic resin is used, and the thick touch on the application surface is insufficient. Comparative Example 7 is inferior in terms of the waxing resistance, the interlayer adhesion, the bubbling critical thickness, the running critical thickness, etc. It is evident from the above that the silicone-modified polyester topcoat paint composition of the present invention has a very desirable performance.

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